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Report No. IITRI C6183-5
Final Report

CHEMICAL SPECIES IN ENGINE EXHAUST AND THEIR CONTRIBUTIONS TO EXHAUST ODORS

National Air Pollution Control Administration
and
Coordinating Research Council

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This project investigated the chemical composition of the odorants in diesel engine exhaust. Exhaust samples were collected in fluidized or packed bed collectors filled with gas chromatographic packings. Separation of the individual compounds was accomplished by two gas chromatograph columns in series. Final identification of the separated compounds was accomplished by mass spectrometry. About 100 compounds were judged to be odor relevant in diesel engine exhaust by this procedure.

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National Air Pollution Control Administration

and

Coordinating Research Council

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FOREWORD

This report presents the work accomplished during the period May 20, 1969, through January 19, 1970, on IITRI Project No. C6183, "Chemical Species in Engine Exhaust and Their Contributions to Exhaust Odors." The progress achieved during the previous year on the same program is incorporated into this report to provide a summary of the two year effort.

Other personnel who contributed to the two year program were Dr. R.G. Scholz, Dr. B.K. Krotoszynski, Mr. A.F. Anderson, Mr. T.A. Burgwald, Mr. E.H. Luebcke, Mr. T.M. Rymarz, Mr. N.S. Shaw, Mr. T.A. Stanley, and Miss J.B. Whitfield.

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ABSTRACT

The nature of odorous species in the exhaust from a Detroit Diesel Engine Division 6V-71N, operated at constant load and fuel conditions, was investigated using high-resolution two column gas chromatography, mass spectrometry on resolved species, and sensory observations. Solid adsorbent collection devices were used to sample from a nitrogen-diluted exhaust stream. Although the presence of many hundreds of compounds was indicated by the chromatograms, only a small fraction were found to exhibit distinct odors at concentrations encountered in the exhaust. The major concentration species, the paraffinic hydrocarbons, are individually non-odorous. The odor-relevant species are polar, and many exhibit low odor thresholds, occurring in the exhaust in relatively small concentrations. From mass spectral data, a variety of compound types was found among the more important odor contributors including: aliphatic aldehydes, aliphatic compounds with more than one position of unsaturation, alkyl derivatives of benzene, indan, tetralin, and naphthalene, aldehyde and ketone derivatives of benzene and alkylbenzenes, and sulfur species. Auxiliary gas chromatographic methods suggested that aliphatic acids are also odor relevant.

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I. INTRODUCTION

The objective of the project was to investigate the nature and identity of molecular species encountered in a diesel exhaust reproducibly available from the same engine operated under the same conditions with the same fuel. Emphasis was placed on those species that by sensory assay were rated as significant odor contributors.

The isolation and identification of the odor-relevant components in diesel exhaust required the application of effective sampling and analysis techniques suitable for handling complex mixtures of organic substances in the presence of a large excess of water vapor. The direct sampling from a nitrogen-diluted exhaust progressed to solid-adsorbent-phase collectors which completely extracted all possibly odor relevant organic vapors from a diluted exhaust flow. Separation of components in the collected sample was achieved by high resolution gas chromatography. Support-coated open tubular columns with Apiezon L and Carbowax 20M stationary phases were used for the initial analyses of exhaust samples in a single column chromatograph which provided for odor analysis in parallel with flame ionization detection.

Further sample resolution and partial component characterization through polarity dispersion were achieved with a two-column chromatograph. The dual-column system comprised two high resolution columns of different polarity, Carbowax 20M and Apiezon L, connected in series, with the option of selecting the portions of the first column effluent to be injected onto the second column. Odor analysis was performed on the effluent from each column. With the two-column chromatograph, sufficient isolation of the odor-relevant species from the bulk of non-odorous components was obtained to allow the selected trapping of odorous compounds for mass spectrometric identification with a specially designed interfacing unit.

II. SUMMARY AND CONCLUSIONS

High-resolution gas chromatographic analysis, sensory assays of gas chromatographically resolved components, and mass spectrometric identification techniques were employed to investigate the nature of chemical species in diesel exhaust. Emphasis was placed on those species which appeared to carry significant odor notes at levels corresponding to their individual concentrations in the exhaust. The source of the exhaust was kept constant; a Detroit Diesel Engine Division 6V-71N, operated with No. 1 diesel fuel at 54 HP and 1200 rpm, served as the source.

The collection and sample enrichment techniques consisted of preferential absorption of organic species by non-polar organic materials followed by recovery at higher temperatures in an inert gas. Each analysis utilized a new sample. Three different collecting phases and several collector geometries were used. Chromosorb 102, a porous polymer, solid-adsorbent medium, proved to be the most efficient collecting phase, providing the capacity for large samples and completely extracting all species of possible odor relevance from the exhaust sampling stream. Complete sample extraction from a known volume of exhaust permitted the extrapolation of odor judgements on species in the gas chromatograph effluent back to odor relevance in the original exhaust.

Gas chromatographic separations utilized Carbowax 20M and Apiezon L support-coated open tubular columns, singly or in tandem in a special two-column gas chromatograph. The presence of organic acids and phenols was explored using a Chromosorb 101 column. A flame ionization detector and sniffing port on the effluent from the columns were used to observe the eluted species and evaluate their odor notes. A flame photometric sulfur detector was employed to scan the gas chromatographic effluent for the presence of sulfur compounds.

Mass spectrometric investigations were conducted on species isolated after passage through the two-column gas chromatograph in which the sample was first resolved in a Carbowax 20M column and

individual multicomponent peaks were further separated in an Apiezon L column. Interpretations on the nature and physico-chemical properties of components were possible on the basis of the positions of peaks in these two columns. Gas chromatographic classifications were reduced to Kovats index notation for ease of cross-referencing. The indexing was facilitated by the presence of n-alkanes in the exhaust; these served as convenient internal standards.

The study produced an inventory of odorous components in diesel exhaust up to an estimated boiling point of 260°C. The following conclusions were drawn:

1. The composition of diesel exhaust was sufficiently complex so that even the resolution obtained with a 200' polar gas chromatographic column with 15,000-20,000 theoretical plates still yielded peaks which were further resolvable into 4 to 20 species in a second non-polar column. At sensitivities sufficient to gas chromatographically represent species present in the exhaust at concentrations above 10^{-13} g/ml, the estimated number of all components exceeds 1000.

2. The majority of the organic species are individually non-odorous at concentrations encountered in the exhaust. Less than 100 species exhibit marked odoros at their respective concentrations. Among the non-odorous components, aliphatic hydrocarbons with at most one double bond seem to account for most of the species. The largest concentrations occur in the range between C_{10} and C_{14} alkane elution times.

3. Aldehydes of the n-series, from ethanal through octanal, were identified mass spectrometrically, and the presence of higher members of the series through undecanal was suggested from sensory and gas chromatographic data. Aldehydic derivatives of benzene, alkyl substituted benzenes, and furan were also identified. The odor notes of the various aldehydes are highly dependent on the nature of the aldehyde, and, therefore, they cannot be considered as an homogeneous sensory class.

4. Alkyl derivatives of benzene, indan, tetralin, and naphthalene were classes of identified components contributing a considerable number of strongly odorous species. These odors were classified as "burnt-pungent."

5. Mass spectral data indicated the presence of aliphatic and cyclic species with more than one position of

unsaturation. These components carried "burnt" odor notes.

6. Specifically foul odors were observed for six species. One was identified as trimethylthiophene. The identity of the others was not clarified but all were strongly polar, indicating oxygenates or highly unsaturated non-oxygenates.

7. Approximately 36 species with burnt (but not exclusively burnt) odor notes were observed. They eluted from the Carbowax 20M column beginning approximately with the C_{11} alkane position and generally tended to be strongly polar. Five species with particularly intense burnt odors were observed in the 160°-180° boiling point range. They possessed very low odor thresholds, occurring in concentrations insufficient for mass spectrometric identification.

8. The presence and odor relevance of the free n-alkanoic acids was confirmed by sensory assay of the gas chromatographic effluent at calibrated retention times. Pure acids with more than nine carbon atoms were judged sufficiently non-odorous to be excluded as contributors to exhaust odor.

9. Since the number of significantly odorous species in diesel exhaust is limited, it appears feasible that valid correlations can be found between the analytical composition and the overall odor intensity and character. However, since the strongly odorous components belong selectively to certain members of a variety of chemical classes of species and diverge in odor character and intensity, an orderly relation between the presences of certain chemical classes (e.g., total aldehydes) and odors cannot be expected. Rather, the correlations should deal with the presence and concentration of certain members of certain chemical classes.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES - DESCRIPTION AND RATIONALE

A. Emission Source

A Detroit Diesel Engine Division 6V-71N with N-60 injectors served as the exhaust gas generator for this study. The engine, rated at 210 HP at 2100 rpm, was operated on #1 Diesel Fuel at 54 HP and 1200 rpm. It was mounted on a bed plate and loaded with a Midwest eddy current dynamometer capable of absorbing 300 HP.

Because the exhaust sampling devices must be operated near ambient temperature, it was necessary to cool the engine exhaust without condensing its water content. By diluting a portion of the exhaust with pure, dry, non-odorous nitrogen, the exhaust temperature was reduced without passing through the dew point. At typical operating conditions, overall fuel to air ratio of 0.172 and intake air at 78°F and 23% relative humidity, and assuming complete combustion of a $C_{14}H_{30}$ fuel, the dew point of the exhaust was calculated to be 87°F. At the 11:1 nitrogen to exhaust dilution ratio used, the calculated dew point of the exhaust sampling stream was below 30°F. Descriptions of the exhaust sampling system, engine and sampling operating conditions, and #1 Diesel Fuel analysis are included in Appendix A.

B. Exhaust Sampling Devices

Three types of sampling devices were used during the project to collect exhaust samples for analysis: fluidized bed samplers, packed bed samplers, and high capacity packed bed samplers. Collection media employed in the samplers were Apiezon L, SF-96, and Chromosorb 102. Characteristics of the sampler types varied, but all permitted a collection and concentration of vapor components suitable for gas chromatographic and odor analysis without water vapor collection. The low affinity of the non-polar collection phases for water eliminated the necessity of additional sample pretreatment, and the small amounts of water

collected did not interfere with later sample transfer and analysis procedures.

The fluidized bed sampler is a glass column containing 10g of 40/60 mesh Fluoropak 80 with a 15% coating of Apiezon L held loosely packed. Diluted diesel exhaust was pulled through the sampler at a rate of 45 l/min. At this sampling rate the bed material is in constant motion (hence the name, fluidized bed), providing good contact between the exhaust and the collector surfaces. During a 30-min sampling period about 1400 liters of diluted exhaust passed through the bed.

The Apiezon L fluidized bed sampler collects each vapor component until an equilibrium is attained between the component concentration in the vapor and in the Apiezon L solution. The concentration factor is dependent upon the partition coefficient for each vapor component. Since the Apiezon L phase is a non-polar material, it exhibits little affinity for water vapor. The effective concentration of less volatile vapor components was the useful property of this sampler.

However, in order to make a judgement on the odor relevance of any particular component in the exhaust, a sampler was needed which would collect all components from a known volume of exhaust. The first samplers of this type employed were packed bed collectors containing 4.2g of 15% SF-96 (a methylsilicone fluid) on 80/100 mesh Chromosorb HP. Two liters of the diluted exhaust were pulled through the collector at a rate of 100 ml/min. For the more polar and more volatile exhaust components,this bed, like the fluidized bed, collects until equilibrium is attained between the vapor phase and solution phase concentrations. For the heavier components, the equilibration concentrations will be greater than the amount present in the gas sampled,so that the entire amount in the sample will be collected. As with the Apiezon L collector phase, water has a limited solubility in SF-96.

Two drawbacks of the SF-96 collector developed during the course of exhaust analysis procedures. First, interpretation of

odor relevance data was difficult because of the fractional collection of some components. Only exact knowledge of the partition coefficients of these components in the SF-96 phase would allow calculation of the original component concentration in the exhaust. Secondly, it became necessary to collect a larger sample because of the sample splittings involved in the gas chromatographic procedures and for mass spectrometric analyses. Increasing the collector capacity by increasing the amount of SF-96 was not a suitable means for increasing sample size, since then water collection began to reach a level where it interfered in the gas chromatographic analysis. Also, larger amounts of water temporarily change the polarity characteristics of the stationary phase with a marked loss in resolution and shift in Kovats Indexes of polar components.

A collector phase of Chromosorb 102 (C-102), a styrene-divinylbenzene copolymer, was adapted for collection of diesel exhaust samples in the packed bed configuration. The material is a solid, porous, non-polar adsorbent with a high collection capacity due to an extremely expanded surface area, 300-400 m^2/g. The following comparison of an SF-96 collector with a C-102 collector of the same physical size (16 cm^3 of packed column) emphasizes the superior collection efficiency of C-102:

	Volume of Vapor Retained at 25°C, ml	
Vapor	SF-96	C-102
Pentane	300	14,000
Methanol	240	2,000
Ethanol	400	12,000

Water vapor retention volume in the C-102 collector is 200 ml at room temperature.

Data available indicated that retentions of various organic compounds in C-102 follow the order of retention times on non-polar silicones, such as Dow Corning 550, in which the Kovats Index of ethanol is approximately 500, similar to n-pentane.

Thus, all compounds with K.I. ≥ 500 would be fully retained from the first 10 liters of sample gas. Tabulations of Kovats Indexes for oxygenates in DC 550 column at 120°C list only the following compounds with Kovats Index below 500: formaldehyde, methyl ether, methanol, acetaldehyde, methyl formate, ethanol (K.I. = 498, already fully retained from 10-l), and ethylene oxide.[1]

The partially collected components from a 10 liter exhaust sample would now include only those polar species more volatile than ethanol and non-polar species more volatile than pentane. Such species have low odor contribution potential. Therefore, the C-102 sampler was assumed to be a satisfactory total collector for all organic species of possible odor interest in the exhaust. Thus, a better judgement of the odor relevance of particular components could be made since extrapolations from component concentrations at the gas chromatograph sniffing ports back to actual concentrations and odor relevance in the original exhaust were possible.

In addition to the superior sample enrichment factor, the C-102 adsorbent is not limited by one inherent defect occurring with absorbent-coated supports. To accumulate in the film of liquid or grease coating the support, the vapor molecules must diffuse through the film material. The rate of this process depends on the diffusion coefficient of the component in the film. It is slow for a film of grease-like Apiezon L and faster for the fluid methyl-silicone, SF-96. However, for an adsorbent such as C-102, this rate limitation is absent. Every molecule impacting on the surface reaches its equilibration site almost instantaneously, except for residual effects caused by a slight diffusion into the structural matrix of the polymer. Thus, faster collection is feasible with the C-102 material. When mass spectrometric analysis of gas-chromatographically-separated exhaust components necessitated

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[1] W.O. McReynolds, "Gas Chromatographic Retention Data," Preston Technical Abstracts Co., Evanston, Illinois, 1966.

the larger samples, a wider diameter C-102 packed-bed sampler was fabricated to permit the collection of a greater amount of exhaust in a reasonable amount of time. A total sample of 100 liters of dilute exhaust (9.1 liters actual exhaust) was collected at a rate of 3 l/min.

Details on the construction of the various collectors used and associated sampling parameters are included in Appendix B.

C. Sample Elution and Injection Techniques

The collected diesel exhaust sample was removed from the various sampler types by reverse flushing with cryogenically purified helium while heating the sampler. Eluted sample was collected in a specially designed injector needle held at liquid nitrogen temperatures during the transfer. The cold injector needle containing the sample was then attached to the chromatograph. The sample was subsequently flash vaporized and injected into the chromatograph with carrier gas. Details of the elution and injection apparatus are included in Appendix C.

The sequence of the collection and transfer steps was found to be reasonably reproducible. Reproducibility was tested by preparing a synthetic mixture of organic vapors in air, including both polar and non-polar species to represent a portion of the range of component types in diesel exhaust. Samples of the mixture were collected in high capacity C-102 samplers, then eluted, injected, and analyzed under the conditions used for exhaust samples. Table I indicates the reproducibility obtained. Using the same synthetic mixture, the efficiency of sample recovery in the 60-min elution period used for exhaust samples is shown to be 90% or better in Table II. Injections of diesel samples after collection in the injector needle consistently proved to be 95-98% complete.

Table I

SAMPLING REPRODUCIBILITY
GAS CHROMATOGRAPHIC ANALYSIS OF THREE SAMPLES
COLLECTED FROM THE SAME SYNTHETIC MIXTURE OF VAPORS
IN HELIUM

Column: 200-ft Carbowax 20M support-coated, open tubular
Analyzed at 2°/min temperature rise

Vapor	Amounts Found (in peak areas, cm^2) Sample 1	2	3
Heptane	3560	3710	3700
Dodecane	22	21	20
Tetradecane	49	50	46
1-Butanol	56	57	59
1-Hexanol	591	602	584
2-Octanone	115	112	120
Propanal	52	50	50
Butanal	11	10	Flow Stopped
Ethyl Butyrate	696	737	690

Table II

HIGH CAPACITY CHROMOSORB 102 NEEDLE COLLECTORS -
EFFICIENCY OF SAMPLE RECOVERY PROCEDURES

Compound	Consecutive 30-Min. Sample Transfers Peak Areas, cm^2 1	2	3	% Recovery in 60-Min.
Heptane	3564.0	294.4	18.6	99.1
Dodecane	22.4	7.7	4.2	88.0
Tetradecane	49.0	0	0	100.0
1-Butanol	56.3	0	0	100.0
1-Hexanol	591.4	44.8	50.0	92.7
2-Octanone	115.2	19.2	16.0	89.4
Propanal	53.6	0	0	100.0
Butanal	10.9	0	0	100.0
Ethylbutyrate	696.3	56.0	12.0	98.4
1-Octanol + Hexadecane	133.4	19.2	15.7	98.0

D. Gas Chromatographic Equipment and Techniques

The study of diesel exhaust for the objective of elucidating odorous components was conducted principally through the application of high resolution gas chromatographic techniques, coupled with provisions for odor analyses and mass spectrometric investigations. Stationary phases of Apiezon L and Carbowax 20M in high resolution columns were used individually in a single column instrument and in unique combination for a two-column chromatograph. The chromatographic techniques provided the capability for sample component separation, thus eliminating the need for additional sample pretreatment procedures.

The single column gas chromatograph was equipped with a sniffing port and a flame ionization detector in parallel to monitor split portions of the column effluent. Two support-coated open tubular (SCOT) columns, 200' by 0.020" i.d., with Apiezon L and Carbowax 20M stationary phases and a packed column, 4' by 3 mm o.d., containing 60/80 mesh Chromosorb 101 were applied to diesel exhaust samples.

Apiezon L is a non-polar phase and retardation of sample components in the column is determined primarily by their boiling points. Retention time in the polar Carbowax 20M column is determined by both the boiling point and the polarity of the components, that is, the interaction of their functional groups with the column material. Thus, on the Carbowax 20M column, polar species are retained longer than non-polar species having similar boiling points. In general, a polar phase such as Carbowax 20M is better suited to samples containing oxygenated species.[2]

The Chromosorb 101 is a non-polar solid adsorbent, a styrene-divinylbenzene polymer resin. It will chromatograph well the lower free fatty acid and phenols. The free acids cannot be chromatographed on either Carbowax 20M or Apiezon L, and phenols will

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[2]A.B. Littlewood, "Gas Chromatography," Academic Press, New York, N.Y., 1962, p. 427.

not chromatograph on Carbowax 20M.[3,4] Thus, the Chromosorb 101 column was applied to exhaust samples to specifically investigate the presence and odor relevance of these two component types.

A diesel exhaust sample was also analyzed on a single column chromatograph equipped with a dual detector system. A flame ionization detector operated in the normal mode and a flame photometric detector specific to sulfur compounds[5] monitored split portions of the effluent from a 20', 0.125" i.d. packed column of 20% Carbowax 20M on 60/80 mesh Chromosorb P.

The two-column gas chromatograph, which was used for the major portion of the exhaust study, consists basically of two high resolution columns of different polarity connected in series, with the option of selecting the particular portions of the first column effluent to be injected onto the second column. This instrumental technique affords two interrelated advantages. The first is the increased resolution, particularly useful for the diesel exhaust samples under study that produced multicomponent peaks even when chromatographed through a high resolution column. The second advantage is the information provided on the nature of individual components from the resultant retention times on the polar - non-polar column set. The unique advantage is that each component can be rechromatographed as it is eluted from one column. In addition, the system is designed to include odor analysis of the effluent from each column for the specific purpose of locating and isolating the odor relevant constituents of the

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[3] ibid., p. 414 ff, p. 436 ff.

[4] H.P. Burchfield and Eleanor E. Storrs, "Biochemical Applications of Gas Chromatography," Academic Press, New York, N.Y., 1962, p. 271 ff, p. 345 ff, p. 527 ff.

[5] Sam S. Brody and John F. Chaney, J. of Gas Chromatography, Feb., 1966, 42-46.

sample. Dual sets of parallel sniffing ports and flame ionization detectors are provided.

Most of the diesel exhaust samples were analyzed in the two-column instrument using a 200', 0.020" i.d., Carbowax 20M SCOT column as the primary column with a 50', 0.020" i.d., Apiezon L SCOT column as the second column. Several samples were analyzed with a reverse column set. The primary column was replaced with a 200', 0.020" i.d., Apiezon L SCOT column and the second column changed to a 50' Carbowax 20M SCOT column, 0.020" i.d.

Specific descriptions of the gas chromatographic equipment and techniques are covered in Appendix D. For all chromatographic analyses of diesel exhaust samples on Carbowax 20M, Apiezon L, and the two column sets, the column temperature was programmed at 2°C/min from 40° to 180°C and isothermal at 180°C thereafter.

In order to correlate the resultant data on diesel exhaust samples for the entire period of study from all the chromatographs used, and to eliminate the effects of slight variations in chromatographic conditions from one analysis to another, the Kovats retention index system was applied to the chromatographic data. The Kovats Index system, described in Appendix E, relates the retention time of a component to a scale determined by the retention times of the n-alkanes. This method of dealing with chromatographic data was particularly suited to diesel exhaust samples since the n-alkanes from hexane through hexadecane were confirmed present in the samples. Thus, the reference points of the Index Scale were available as internal standards. For indexing above hexadecane, n-alkane standards were added to the samples. From the n-alkane reference points, under the linear temperature program conditions used, a calibration curve was obtained. The Kovats Indexes of all other sample peaks were interpolated from this curve using computer programs also described in Appendix E.

E. Gas Chromatographic - Mass Spectrometer Interfacing

For the task of identifying odor relevant components in the exhaust by mass spectrometry, a GC-MS interfacing device was developed for the particular requirements of the diesel exhaust sample. Because of the complexity of the sample, the two-column chromatograph was needed to provide sufficient resolution of components by rechromatographing odorous Carbowax 20M peaks on the Apiezon L column. The resultant Apiezon L chromatograms of individual Carbowax 20M peaks generally showed several components, particularly many aliphatic hydrocarbons, but sufficient separation of the one or more odorous species in the peak was achieved. Only these odor-relevant components were required for mass spectrometric analysis.

The entire interfacing device was designed to incorporate the following features:

1. The capability of rejecting peaks in the Apiezon L chromatograms, trapping only the odorous peaks of interest.
2. Discrete stations for cryogenically trapping individual peaks and later releasing the peak for mass spectrometric analyses by heating the same trapping area.
3. A small volume system, relying only on the pumping speed of the mass spectrometer to transfer trapped components from the interface to the mass spectrometer. Because the distance travelled at the low leak rate diffused the trapped components during transfer, the peaks were retrapped at the entrance to the ion chamber in order to inject them into the MS in good peak form.
4. A closed system when attached to either the gas chromatograph or the mass spectrometer, avoiding any contamination of sample during the process of detachment from the former and connection to the latter.

A detailed description of the design and operation of the interfacing assembly is presented in Appendix F. The mass spectrometer used in the diesel exhaust study was the Hitachi Perkin-Elmer magnetic scanning Model RMU-6D.

F. Experimental Basis for Sample Component Characterization

The purpose of this diesel exhaust study was to elucidate and characterize those components in the exhaust which are odor relevant. The question of odor relevancy hinged on the effectiveness of the entire sampling procedure, so that the odor judgements made on sample components by monitoring the chromatograph sniffing ports could be related back to odor relevancy in the original exhaust. Exhaust sampling required the total collection sampler and efficient transfer and injection techniques described in the above sections. The following calculation demonstrates the relation between sniffing port concentration and original exhaust concentration for a component using a 10 liter diluted exhaust sample collected on the Chromosorb 102 sampler and analyzed on the two-column gas chromatograph.

A component in the original exhaust at a concentration of w g/ml results in a sample concentration of 910w g when 10 liters of 11:1 diluted exhaust are collected. Assuming a 90% efficiency for sample transfer and injection and considering the sample splitting in the chromatograph, which delivers 25% of the injected sample to each sniffing port, then approximately 200w g of the component reaches the sniffing port. This concentration elutes from the chromatograph in 30-40 seconds (average peak width) with 30-40 ml of the helium-humidified air mixture (60 ml/min flow). Thus, the odor of the component is monitored at a concentration of 5 w g/ml, or about five times the concentration in the original exhaust. From detector sensitivity calibrations, any component occurring in the exhaust at concentrations greater than 1×10^{-13} g/ml will produce a noticeable peak on the chromatograms from a 10 liter sample of diluted exhaust.

With the two-column instrument, equipped with a sniffing port at each column exit, components in the exhaust sample that were odor relevant could be isolated. Odorous areas in the Carbowax 20M chromatogram were rechromatographed on the second column and the odorous components identified from among the Apiezon chromatogram peaks. In addition, inherent in this isolation process is a partial characterization of the unknown sample components.

Obtaining retention data for a component on two different stationary phases is the basis of the characterization technique.

The retention time of a component on Carbowax 20M is determined by the combination of a component's boiling point and polarity, whereas the Apiezon L retention time is determined primarily by boiling point only. In effect, the amount of retardation in the second Apiezon column will define the degree of polarity of a component. When a multicomponent peak in the Carbowax 20M effluent, which may be composed of a range of polar, lower boiling components to non-polar, higher boiling components, is injected onto the second column, the Apiezon L dispersion will be a functional group separation. The two-column data obtained permits an estimation of the retention index difference, ΔI, of Kovats Index notation. By the thermodynamically based Kovats Index rules, the ΔI is characteristic of the structure of a substance, the combined effect of the functional group and skeletal structure of the molecule.

In order to calibrate the polarity dispersion resulting from the two-column technique, several types of standards were run under the same experimental conditions used for sample analysis. Table III lists the two-column data for the calibration standards. The retention time data on Carbowax 20M is converted to Kovats Indexes. Conversion of the Apiezon L data to Kovats Indexes is not possible, so the corrected retention times are used. The homologous series of n-alkanes define the maximum retention times possible in Apiezon L chromatograms throughout the range of the Carbowax 20M chromatogram since no species could be more non-polar and thus could not experience greater retardation. These n-alkane retention limits define the time interval that must be maintained between successive injections of Carbowax 20M effluent onto the second column. After this delay time from the peak injection point, all possible components have eluted from the Apiezon L column. The homologous series of 1-alcohols represent the species, among single functional group types, that would experience minimum retardation. The presence of more than one functional group, of course, will add to the polarity and thus reduce the retardation.

Table III

TWO-COLUMN CHROMATOGRAPH CALIBRATION DATA FROM STANDARDS

Compound	Kovats Index Carbowax 20M	Retention Time[a] Apiezon L (min)
Pentane	500	0.37
1-Pentene	536	0.30
3-Methylpentane	570	0.62
2-Pentene	571	0.43
Hexane	600	1.03
1-Hexene	642	0.85
2,2,4-Trimethylpentane	653	2.11
2-Hexene	670	1.07
Heptane	700	2.50
Cyclohexane	719	2.41
Dimethylhexane	723	3.15
1-Heptene	740	2.10
3-Heptene	743	2.33
2,3,4-Trimethylpentane	756	3.72
2,3,5-Trimethylhexane	764	4.04
Propanal	792	0.40
Octane	800	4.97
1,2-Epoxybutane	826	0.64
1-Octene	830	3.95
2-Methyltetrahydrofuran	858	1.22
2-Ethyl-1-hexene	860	4.09
Methanol	862	0.34
2-Octene	870	4.10
Butanal	871	0.60
2-Propanol	883	0.29
Diethylsulfide	889	1.35
2-Butanone	893	0.44
2,5-Dihydrofuran	897	0.69
Nonane	900	7.40
Tetrahydropyran	910	1.53
Ethanol	912	0.43
2-Methyltetrahydropyran	918	2.00
Benzene	920	1.12
Dihydropyran	925	1.21
1-Nonene	931	5.43
Ethyl-n-propanoate	946	0.76
2-Pentanone	966	0.70
Pentanal	970	0.79
Thiophene	984	0.96
Decane	1000	8.86
Ethyl-n-butanoate	1023	1.16
Toluene	1025	1.72
2-Butenal	1027	0.48
n-Propyl-n-propanoate	1033	1.30
2-Octyne	1034	2.50
1-Decene	1035	6.38
Di-n-propylsulfide	1060	2.74
Hexanal	1070	1.18
Furaldehyde	1075	0.91
Undecane	1100	9.40
n-Propyl-n-butanoate	1110	1.69
Ethylbenzene	1112	2.14
1-Butanol	1118	0.55
Ethyl-n-pentanoate	1123	1.53
p-Xylene	1124	2.32
Nitromethane	1130	0.09
m-Xylene	1130	2.27
2-Heptanone	1170	1.30
Heptanal	1175	1.41
Methyl-n-hexanoate	1175	1.46
Cyclopentanone	1176	0.75
o-Xylene	1176	2.20
Dodecane	1200	9.61
n-Propyl-n-pentanoate	1209	2.05
Ethyl-n-hexanoate	1223	1.88
1-Pentanol	1225	0.80
1,3,5-Trimethylbenzene[b]	1227	2.60
1-methyl-2-ethylbenzene[b]	1242	2.40
1-methyl-3-isopropylbenzene[b]	1248	2.77
1-methyl-4-isopropylbenzene[b]	1248	2.92
Di-n-butylsulfide	1257	3.72
1,2,4-trimethylbenzene[b]	1262	2.57
2-Octanone	1275	1.58
Methyl-n-heptanoate	1276	1.76
Octanal	1280	1.72
1,3-Diethylbenzene[b]	1281	2.85
1-Methyl-3-n-propylbenzene[b]	1284	2.87
Cyclohexanone	1288	1.02
1-Methyl-4-n-propylbenzene[b]	1289	2.92
1,4-Diethylbenzene[b]	1297	2.90
Tridecane	1300	9.83
1,3-Dimethyl-5-ethylbenzene[b]	1300	2.80
n-Propyl-n-hexanoate	1308	2.35
1,2,3-Trimethylbenzene	1320	2.39
Ethyl-n-heptanoate	1323	2.18
1-Hexanol	1331	1.03
4-Methylcyclohexanone	1338	1.22
1,1-dimethylindan[b]	1363	2.90
Cyclohexanol	1380	0.81
Methyl-n-octanoate	1380	2.02
Nonanal	1387	2.00
Tetradecane	1400	10.03
n-Propyl-n-heptanoate	1409	2.63
Ethyl-n-Octanoate	1425	2.49
1-Heptanol	1438	1.23
2-Furaldehyde	1467	0.63
Methyl-n-nonanoate	1483	2.29
Decanal	1494	2.27
Pentadecane	1500	10.28
n-Propyl-n-octanoate	1511	2.91
Furfurylacetate	1520	0.65
Benzaldehyde	1527	0.74
Ethyl-n-nonanoate	1527	2.75
1-Octanol	1547	1.44
Methyl-2-furoate	1573	0.55
Tetrahydrofurfurylacetate	1573	1.05
Methyl-n-decanoate	1587	2.53
1,1,4,6-Tetramethylindan[b]	1587	3.41
Undecanal	1600	2.57
Hexadecane	1600[c]	11.74
Tetrahydrofurfurylpropionate	1643	1.13
p-Tolualdehyde	1658	0.96
Acetophenone	1659	0.83
2,6-dimethyltetralin[b]	1669	3.61
Heptadecane	1700	15.8
Octadecane	1800	24.0
2,2,5,7-Tetramelhyltetralin[b]	1811	6.10
2,5,8-Trimethyltetralin[b]	1884	6.69
Nonadecane	1900	37.8

[a]Apiezon L retention time is corrected for column dead volume.

[b]Hydrocarbon standards supplied by Mobil Research and Development Corporation.

[c]After Kovats Index 1600 the temperature program has ended and the temperature is maintained at 180°C.

For example, 2-butenal, at Kovats Index 1027, with the addition of a double bond functional group to the aldehyde functional group shows the effect of increased polarity over n-butanal, Kovats Index 871, by its later elution from Carbowax 20M and its shorter retention time in Apiezon L.

Figure 1 shows some of the calibration data in a two dimensional plot that illustrates how the information points of a Kovats Index in the first column and a retention time in the second column can result in structure information. The connected data points delineate particular functional groups areas throughout the range of the Carbowax 20M chromatogram. Vertical columns would represent Apiezon L chromatograms (or the dispersion) that would be obtained by switching onto the second column portions of the Carbowax 20M effluent containing components having a retention time on Carbowax 20M identified by the Kovats Index at the base of the column.

Although polarity characterization from the two-column method was stressed, it is also true that other information is inherent in the data obtained and can be correlated with the two-column data. Other molecular properties, such as boiling points, could be represented as the third dimension in Figure 1 and also applied to unknown sample analysis. Iso-boiling point lines are shown in Figure 1. Appendix G describes the investigation of physicochemical properties taken for correlation analyses using the standard data of Table III.

A portion of the exhaust sample work on the two-column instrument was performed with Apiezon L as the primary column and Carbowax 20M as the second column. Although the non-polar phase is less suitable for samples containing oxygenated species, as cited in Section II D, the change in elution order of sample components provided an "odor chromatogram" for comparison with the odor notes from the analysis with Carbowax 20M as the primary column. On Apiezon L, more polar species were eluted before the major portion of aliphatic hydrocarbons in the sample. However,

Approximate column temperatures and Carbowax 20M retention times associated with the designated Kovats Indexes:

Column temperature, °C

53	58	69	83	99	115	130	145	158	170

Carbowax 20M retention time (min) under temperature rise of 2°C/min from 40° to 180°C

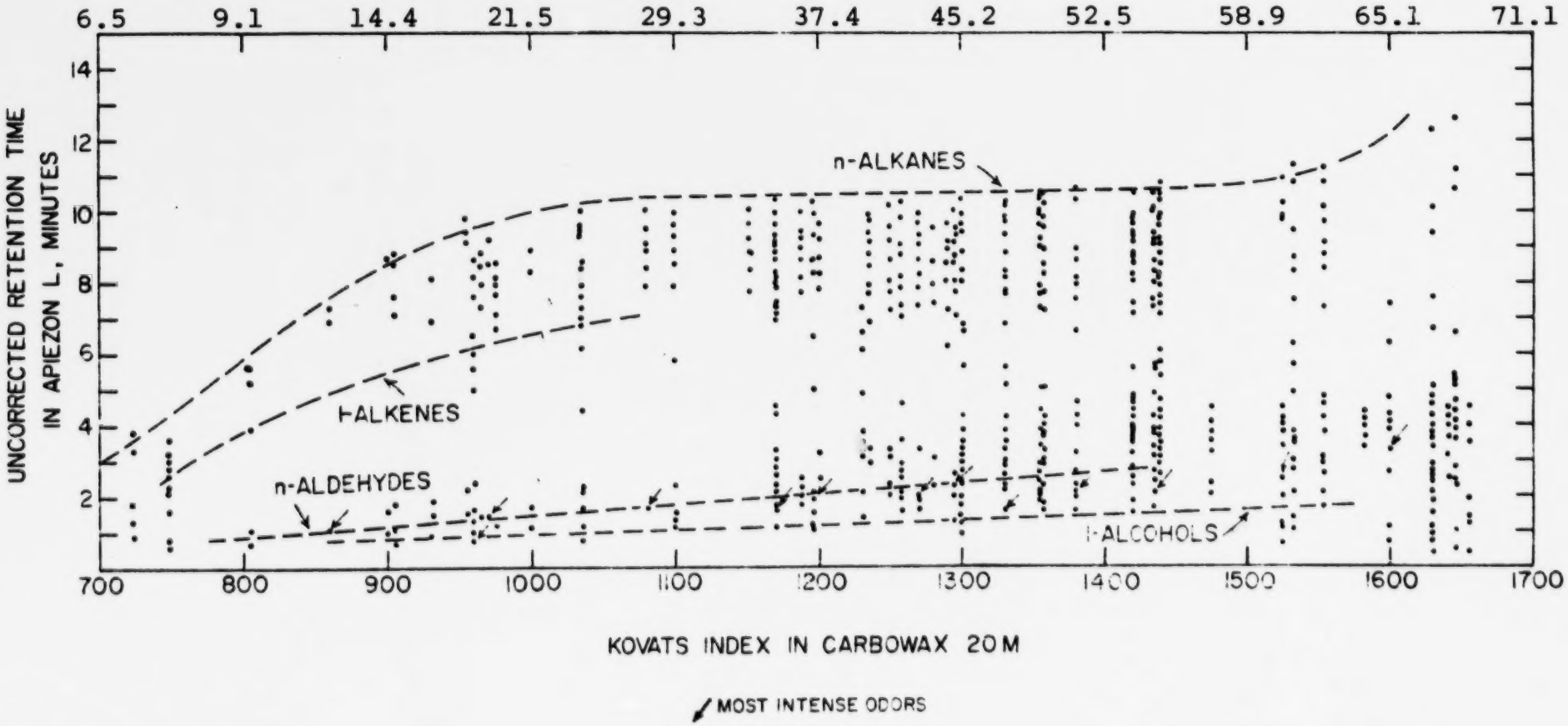

Fig. 1. ANALYSIS OF DIESEL EXHAUST IN TWO-COLUMN CHROMATOGRAPH

the retention dispersion obtained on Carbowax 20M for peaks injected from the Apiezon L effluent was much poorer than that obtained with the original column sequence. Table IV lists calibration data on some n-alkanes and n-aldehydes as examples of the range of retardation for non-polar vs. polar species on the secondary Carbowax 20M colunn. Comparison of this data with the data on the same compounds in Table III demonstrates that the dispersion possible on this column set is not sufficient either for definitive assignments of polarity ranges for component characterization or for the resolution needed for mass spectrometric studies.

Table IV

RETENTION DISPERSION ON CARBOWAX 20M
FOR COMPONENTS ELUTED FROM APIEZON L

	Retention Time Apiezon L, min	Kovats Index Apiezon L	Retention Time* Carbowax 20M, min
Pentane	7.1	500	0.1
Propanal	7.1	500	1.0
Butanal	10.4	572	1.2
Hexane	12.2	600	0.1
Pentanal	18.1	672	1.4
Heptane	20.8	700	0.1
Octane	31.5	800	0.1
Heptanal	39.7	875	1.0
Nonane	42.4	900	0.1
Decane	52.9	1000	0.1
Undecane	62.6	1100	0.1
Dodecane	71.8	1200	0.1
Tridecane	81.6	1300	0.15
Tetradecane	95.1	1400	0.25
Pentadecane	115.8	1500	0.5
Hexadecane	148.6	1600	0.8

*Retention time is corrected for column dead volume.

IV. RESULTS AND DISCUSSION

A. Single Column Chromatograph Studies

The analysis of diesel exhaust samples on the single column chromatograph concentrated on odor characterization. During sample analysis, an observer monitored each effluent peak for odor. The observers were familiarized with the Turk diesel reference odors[6] and were asked to adhere to this classification (aldehydic, pungent, oily, burnt), if possible, in their odor characterizations. Since a number of observers contributed to the diesel sample odor characterization, some odor quality references were necessary in order to correlate the odor data. The majority of the odor annotations were covered by the Turk classifications, although an observer often characterized an "identifiable" odor through his own experience or frame of reference.

One observer was used for an entire sample chromatogram, usually a 70 min analysis extending to the end of the temperature program and encompassing a Kovats Index range through 1600 (hexadecane). A series of samples collected on both Apiezon L fluidized beds and SF-96 packed beds were chromatographed on both the Carbowax 20M column and then the Apiezon L column in the single column chromatograph. Figure 2 presents a typical chromatogram from the Carbowax 20M column of an Apiezon L fluidized bed sample. A typical Apiezon L chromatogram, also from a sample collected on a fluidized bed, is shown in Figure 3.

For the Carbowax 20M chromatograms, the Turk classifications covered about 91% of all peaks for which a descriptive term was used by the observers. For the Apiezon L column analyses, about 62% of the descriptive terms were Turk annotations. Many peaks were simply labeled "odorous" because the rapid elution of peaks did not allow much time for each individual odor

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[6] Amos Turk, "Selection and Training of Judges for Sensory Evaluation of the Intensity and Character of Diesel Exhaust Odors," Public Health Service Publication No. 999-AP-32.

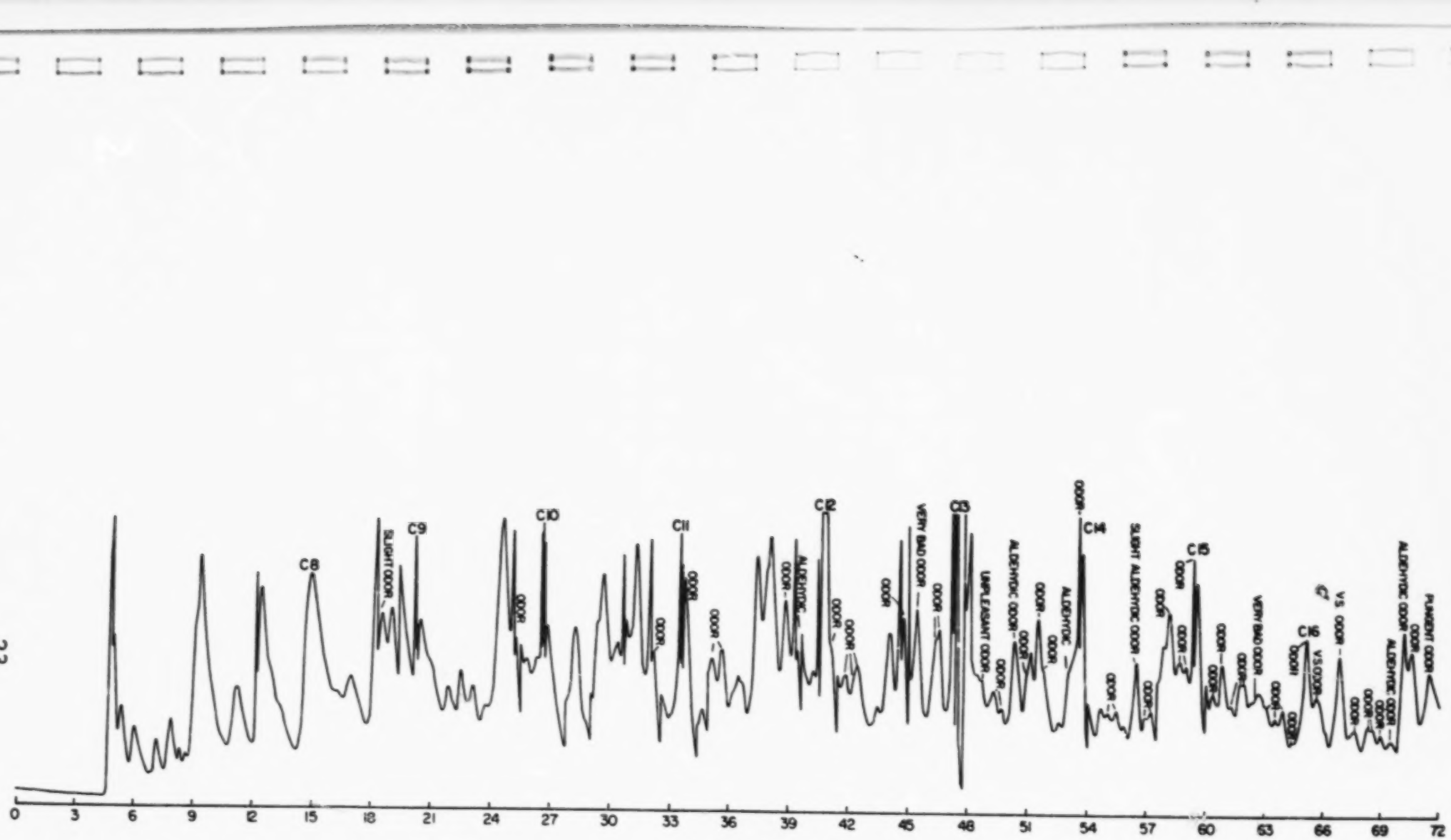
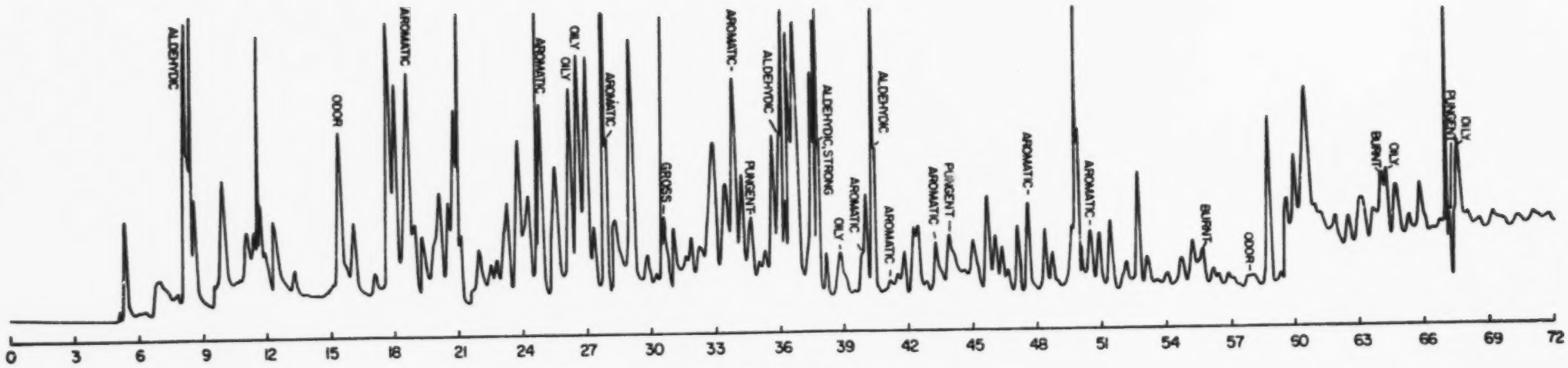


Fig. 2 TYPICAL CARBOWAX 20M CHROMATOGRAM OF DIESEL ENGINE EXHAUST



Engine Run No. 8, Feb. 2, 1969, Fluidized Bed No. 4

Fig. 3 TYPICAL APIEZON L CHROMATOGRAM OF DIESEL ENGINE EXHAUST

judgment. The frequency with which the various descriptive terms were used to characterize the odor quality of the odorous peaks is presented in Table V.

The odor characterization data from the single column Carbowax 20M and Apiezon L chromatograms are summarized in Tables VI and VII, respectively. The summary divides the chromatograms into small Kovats Index ranges. The designated odorous areas of the chromatograms served as reference points for the further isolation and characterization of odorous components using the two-column chromatograph.

B. Initial Two-Column Chromatograph Studies on Fluidized Bed-Collected Samples

Most of the diesel exhaust samples initially analyzed with the two-column instrument were collected on Apiezon L fluidized beds. The primary column Carbowax 20M chromatograms showed good reproducibility both among different bed samples from the same engine test and among different engine tests. The reproducible nature of the sample was a required condition for the systematic investigation of the sample with the two-column system because: (1) it was necessary to predetermine the effluent peaks to be switched onto the second column (split portions of the first column effluent simultaneously entered the second column and reached the first column detector); and (2) only five to seven peaks could be switched per sample run to obtain complete Apiezon L chromatograms of each peak, so many samples had to be analyzed. Figure 4 shows a typical two-column chromatogram from a fluidized bed-collected exhaust sample. Shaded areas on the upper Carbowax 20M chromatogram indicate the peaks injected onto the Apiezon L column. The extent of each Apiezon L chromatogram is marked from the point of injection to the point of maximum permissible elution time for each injection. Odorous peaks on the Apiezon L chromatograms are also indicated. Three sets of duplicate Apiezon L chromatograms are shown in Figure 5, representing Kovats Index peaks at 1420,

Table V

FREQUENCY OF ODOR DESCRIPTIONS

Single Column Data

Descriptive Term	Frequency, %[2] C20M	APL
aldehydic	20.2	10.4
pungent	15.0	21.7
burnt	16.3	11.0
oily	10.2	6.5
smoky	1.6	1.2
musty	0.2	3.5
sour	1.2	0.2
sweet, pleasant	1.4	2.0
foul, unpleasant	2.0	8.0
paraffinic, naphtha, etc.	0.8	3.0
diesel	0.2	0.1
grassy	0.0	1.5
minty	0.0	0.5
misc. odors[1]	0.0	9.5
uncharacterized odors	30.9	20.8

[1] a conglomeration of many descriptive terms such as paint, plastic, latex, vinyl, soap, fruity, fishy, leather, camphor and others.

[2] Frequency of term usage to describe odorous peaks eluted from indicated chromatographic partition column.

Table VI

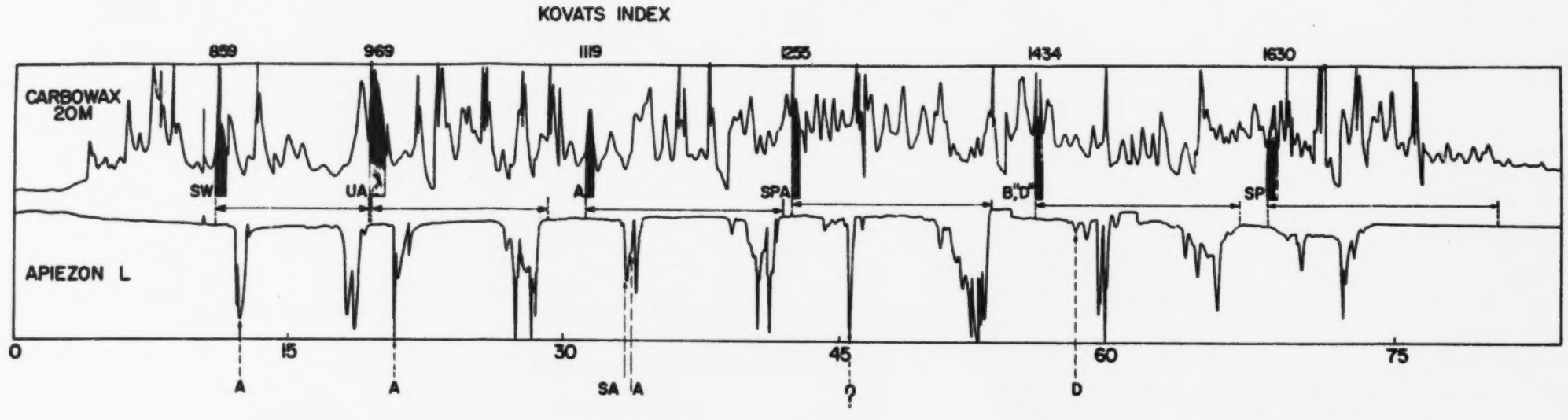
ODOR CHARACTERIZATION BY KOVATS INDEXES
SINGLE 200-ft C20M COLUMN

Kovats Index	Number of Times Descriptive Term Used				
	Ald.	Pung.	Burnt	Oily	Foul
700- 720	0	2	1	1	0
721- 740	2	1	0	0	0
741- 760	0	0	1	1	0
761- 780	0	0	0	1	0
781- 800	1	2	0	1	0
801- 820	3	1	1	0	0
821- 840	0	1	0	2	0
841- 860	1	0	0	1	0
861- 880	1	0	0	0	0
881- 900	1	0	1	0	0
901- 920	2	1	1	1	0
921- 940	4	0	1	0	0
941- 960	2	2	3	0	0
961- 980	4	2	0	3	0
981-1000	1	1	2	1	2
1001-1020	0	1	1	0	0
1021-1040	3	0	3	0	0
1041-1060	2	2	1	0	0
1061-1080	3	5	1	0	0
1081-1100	3	2	1	4	0
1101-1120	4	1	0	2	0
1121-1140	0	0	0	0	0
1141-1160	3	2	0	2	0
1161-1180	3	1	0	1	2
1181-1200	3	2	0	3	0
1201-1220	1	1	4	0	0
1221-1240	4	3	5	0	0
1240-1260	4	1	1	0	2
1261-1280	4	2	0	3	0
1281-1300	10	2	2	1	1
1301-1320	6	2	0	2	1
1321-1340	2	3	2	0	0
1341-1360	2	1	3	2	0
1361-1380	1	4	3	3	0
1381-1400	0	1	6	2	0
1401-1420	6	2	3	1	0
1421-1440	4	3	1	1	0
1441-1460	0	0	4	4	0
1461-1480	0	0	4	1	0
1481-1500	2	1	4	0	0
1501-1520	2	4	4	1	0
1521-1540	4	1	4	2	3
1541-1560	0	4	5	0	0
1561-1580	0	1	3	0	0
1581-1600	2	1	3	6	1

Table VII

ODOR CHARACTERIZATION BY KOVATS INDEXES
SINGLE 200-ft A[illegible] COLUMN

Kovats Index	Number of Times Descriptive Term Used				
	Ald.	Pung.	Burnt	Oily	Foul
700- 720	1	5	1	0	0
721- 740	8	5	1	1	0
741- 760	4	8	2	8	0
761- 780	11	7	0	1	2
781- 800	0	8	0	2	0
801- 820	2	7	1	0	1
821- 840	12	6	0	0	0
841- 860	4	12	4	2	3
861- 880	16	4	2	2	1
881- 900	6	8	1	3	5
901- 920	4	15	1	1	0
921- 940	12	2	2	0	0
941- 960	3	11	2	1	8
961- 980	13	9	2	0	4
981-1000	4	10	2	1	1
1001-1020	4	7	1	1	0
1021-1040	3	7	4	2	5
1041-1060	4	12	3	0	14
1061-1080	11	6	14	1	4
1081-1100	1	3	5	1	0
1101-1120	1	7	4	2	1
1121-1140	0	13	8	2	7
1141-1160	6	10	8	0	1
1161-1180	2	8	6	5	3
1181-1200	2	8	9	2	3
1201-1220	1	6	2	2	3
1221-1240	0	5	3	6	0
1241-1260	0	7	4	3	1
1261-1280	1	2	3	1	2
1281-1300	0	4	3	2	0
1301-1320	0	4	0	1	1
1321-1340	0	2	0	1	1
1341-1360	0	0	0	1	0
1361-1380	0	1	0	1	0
1381-1400	0	2	1	2	0
1401-1420	0	1	0	0	0
1421-1440	0	1	0	0	1
1441-1460	0	0	1	0	0
1461-1480	0	3	0	0	0
1481-1500	0	0	0	1	0
1501-1520	0	0	0	0	0
1521-1540	0	0	0	0	0
1541-1560	0	0	0	0	0
1561-1580	0	0	0	0	0
1581-1600	0	0	0	0	0



ENGINE RUN No.11, FEB. 24, 1969. FLUIDIZED BED No.7

A ALDEHYDIC
VA UNPLEASANT ALDEHYDIC
SA STRONG ALDEHYDIC
SPA SLIGHTLY PUNGENT ALDEHYDIC
B"D" BURNT, DIESEL-LIKE
D DIESEL-LIKE
SP SLIGHTLY PUNGENT
SW SWEATY, ALDEHYDIC

Fig. 4

TYPICAL DUAL-COLUMN CHROMATOGRAM OF DIESEL ENGINE EXHAUST

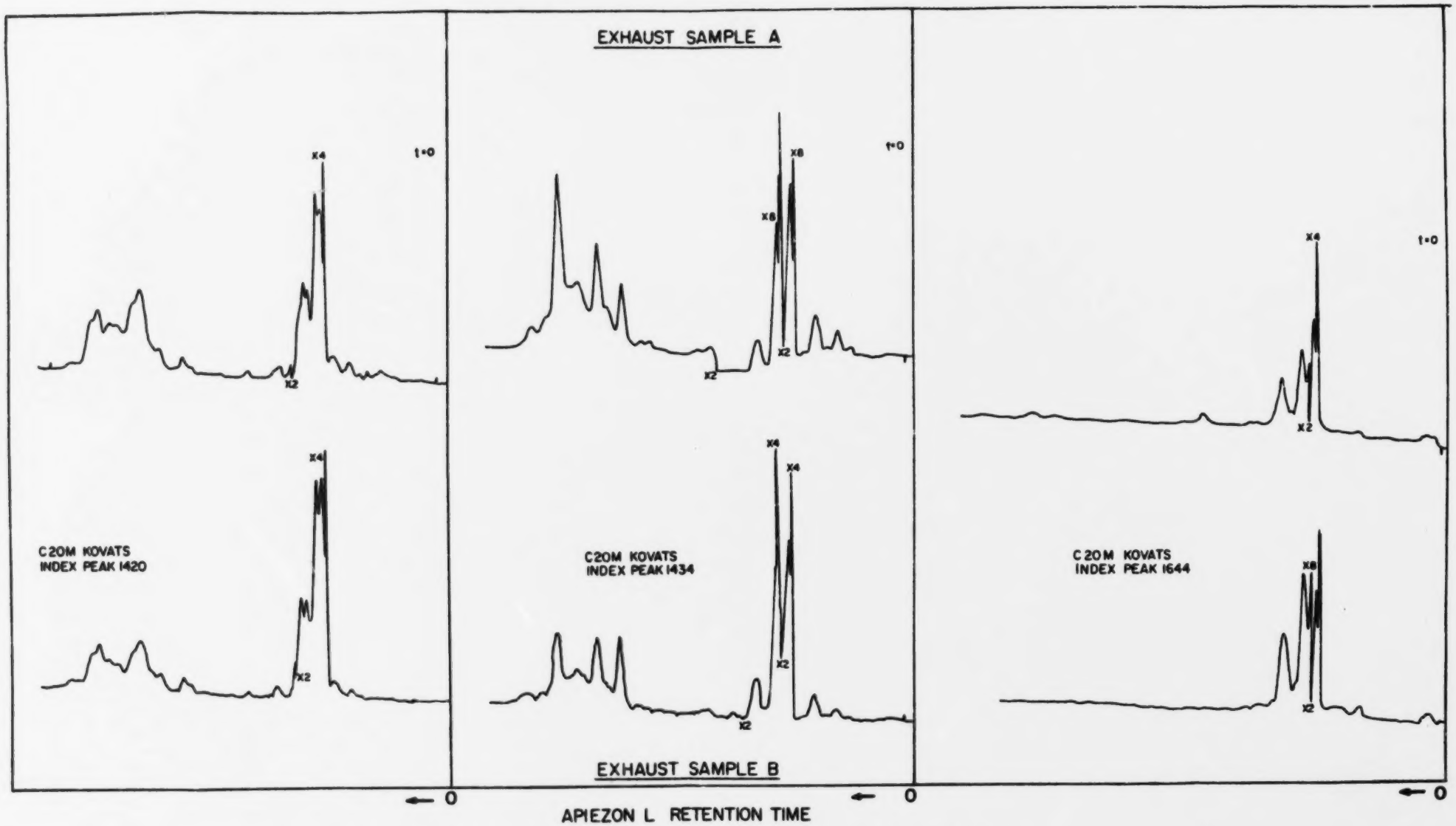


Fig. 5 REPRODUCIBILITY OF DUAL-COLUMN CHROMATOGRAPH

SINCE THE EXHAUST SAMPLES WERE COLLECTED ON DIFFERENT DAYS, THE DATA PRESENTED ILLUSTRATES THE EXCELLENT REPRODUCIBILITY OF ALL PROCEDURES FROM ENGINE OPERATION TO CHROMATOGRAPHIC PERFORMANCE, INCLUDING THE SAMPLING. TRANSFER AND INJECTION PROCEDURES

1434, and 1646 on Carbowax 20M. Members of each pair represent different fluidized bed samples from different engine tests to demonstrate that reproducible exhaust samples were obtained.

The two-column analysis of odorous components from fluidized bed samples concentrated on those species which appeared on the Carbowax 20M chromatograms between Kovats Indexes 600 (hexane) and 1600 (hexadecane). The analyses aimed at finding on the Apiezon L chromatograms the single peak producing the same odor in quality and intensity as the Carbowax 20M peak, if such a component were present, or else noting the odor-contributing peaks which appeared. Every peak rechromatographed resulted in a multicomponent Apiezon L chromatogram, including, in almost all cases, several aliphatic hydrocarbon components. The system effectively separated these hydrocarbon species, which were determined to be individually odor irrelevant, from the odorous components that occurred in low Apiezon L retention time areas.

A partial characterization of the nature of the exhaust sample is evident from a plot of some of the two-column data in a polarity dispersion graph of Carbowax 20M Kovats Indexes against Apiezon L retention times as shown in Figure 6. The points in each vertical column are the Apiezon L chromatogram peaks resulting from the Carbowax 20M peak identified by the Kovats Index at the base of the column. The odor relevant Apiezon L peaks are indicated. Dashed lines representing the calibration data from Figure 1 identify some functional group retention areas. The complexity of the exhaust sample is apparent. Figure 6 also graphically illustrates the capability of the two-column chromatograph technique for analyzing a sample of such complexity.

From the two-column studies, the total number of components was estimated to exceed a thousand. Those components which are odor relevant constitute a very small portion of the diesel exhaust. Table VIII lists all the odorous Carbowax 20M

Approximate column temperatures and Carbowax 20M retention times associated with the designated Kovats Indexes:

Column temperature, °C

53 58 69 83 99 115 130 145 158 170

Carbowax 20M retention time (min) under temperature rise of 2°C/min from 40° to 180°C

6.5 9.1 14.4 21.5 29.3 37.4 45.2 52.5 58.9 65.1 71.1

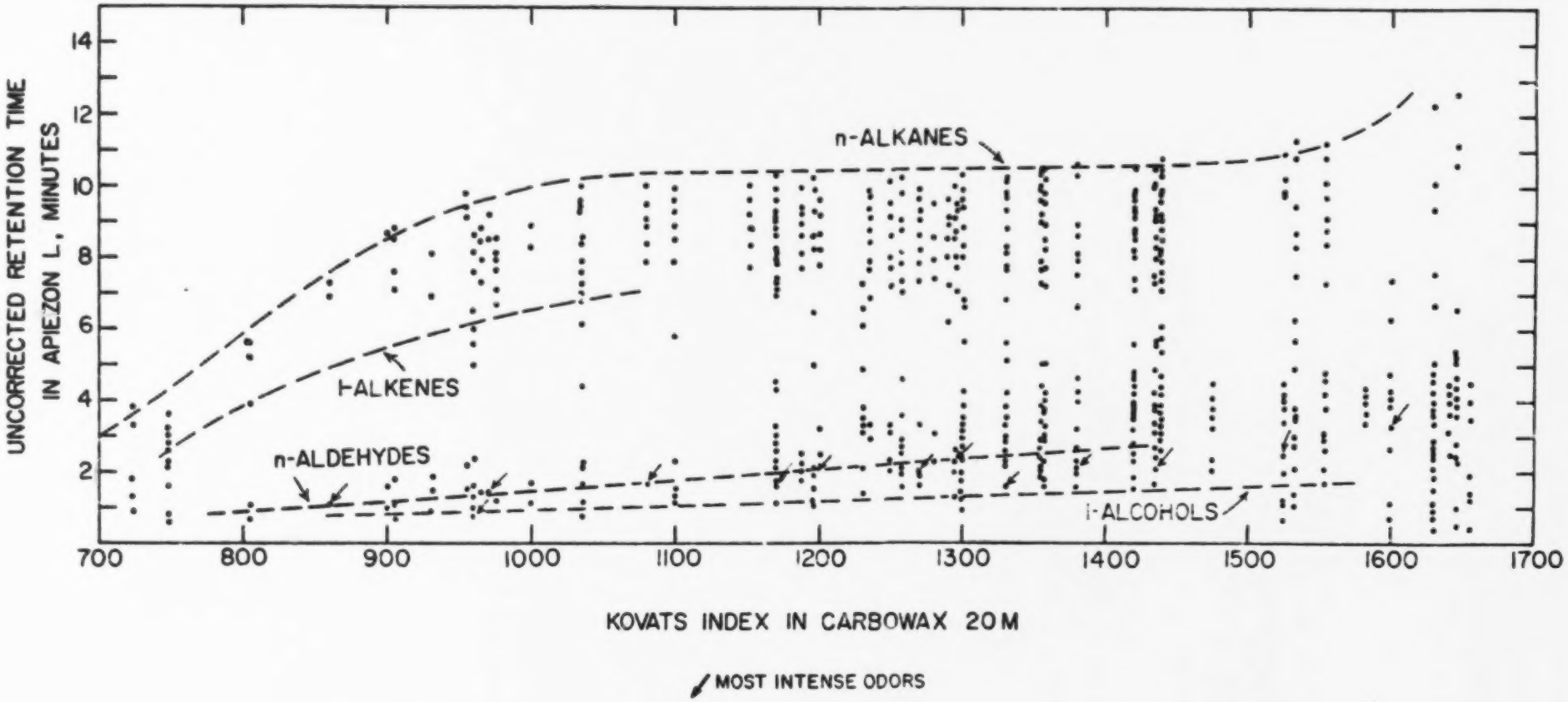


Fig. 6. ANALYSIS OF DIESEL EXHAUST IN TWO-COLUMN CHROMATOGRAPH

Table VIII

SUMMARY OF ALL ODOROUS PEAKS ON PRIMARY COLUMN CARBOWAX 20M CHROMATOGRAM
DUAL-COLUMN CHROMATOGRAPH

Kovats Index Carbowax 20M	Odor Note
723	alcohol
746	alcohol
787*	sweet-alcohol
815	sweaty
852*	sweaty aldehyde
857	sweaty aldehyde
864	sweaty
875	sweaty
879	unpleasant
895	odor
934	very unpleasant, "foul"
953	unpleasant aldehyde
959	unpleasant aldehyde
963*	unpleasant aldehyde
969	unpleasant aldehyde
977	unpleasant aldehyde
1024	pleasant
1031	sweaty aldehyde
1035	sweaty aldehyde
1039	sweaty
1066	pleasant
1073	aldehyde
1078*	strong aldehyde
1095	odor
1100	odor (diesel, oily, aldehyde)
1116	aldehyde
1119	aldehyde
1123	oily aldehyde
1148	odor
1152	pleasant
1159	unpleasant aldehyde
1161	unpleasant
1169	very "foul"
1177*	strong aldehyde
1180	aldehyde
1186	burnt, unpleasant
1192	pungent
1194	burnt
1203	odor
1214	pleasant
1218	pleasant, aldehyde, pungent
1225	burnt aldehyde
1231	pungent aldehyde
1237	strong aldehyde
1239	aldehyde
1245	odor, diesel-like
1249	aldehyde
1255	aldehyde
1260	pungent
1269	very "foul"
1275	odor
1281*	strong aldehyde
1288	sweet
1295	unpleasant, burnt, "diesel"
1300	odor
1308	pungent aldehyde
1316	odor
1319	burnt, pungent, oily, aldehyde
1324	burnt
1329	strong burnt
1331	pungent burnt
1339	sweet, pungent
1342	aldehyde
1347	burnt pungent
1355	burnt, pungent, aldehyde
1357	burnt
1363	odor
1369	aldehyde
1373	burnt, pungent, aldehyde
1379	odor
1382	unpleasant burnt
1387*	sharp aldehyde
1395	unpleasant burnt
1400	unpleasant burnt
1403	burnt "diesel"
1407	pungent burnt
1420	pungent burnt
1425	pungent
1434	burnt, "diesel", pungent
1442	very pleasant
1445	very pleasant
1455	burnt
1457	burnt
1464	unpleasant, "foul"
1469	odor
1478	unpleasant burnt
1484	unpleasant burnt
1489	burnt
1494*	pungent aldehyde
1500	burnt, "diesel", oily
1504	burnt, "diesel"
1510	odor
1518	slight burnt
1525	slight burnt
1532	pungent burnt
1535	pungent aldehyde
1552	pungent burnt
1555	burnt
1560	pungent
1567	slight burnt
1572	sharp burnt
1578	burnt, pungent, aldehyde
1583	burnt pungent
1588	burnt pungent
1594	burnt
1600	burnt, "diesel"
1613	pungent aldehyde
1620	pleasant
1627	pungent
1630	slight burnt
1637	burnt pungent
1644	burnt
1657	very pleasant

*n-aldehyde series, propanal through decanal, identified by comparison of their Kovats Indexes on C20M and their retention time in APL with calibration data.

peaks compiled from the fluidized bed samples analyzed during this period of study.

The largest group of components in terms of concentration were the n-alkanes. Peak sizes indicated that C_8 (octane) through C_{14} (tetradecane) contributed the major concentrations, with the maximum around C_{11} and C_{12}. In terms of odor contribution, the most important group, in number and in odor intensity, was the aldehydic odor type. From Kovats Index rules and calibration data, the homologous series of n-aldehydes from propanal through undecanal were identified. Other aldehydic odor peaks were found clustered around the n-aldehyde peaks, and a second aldehydic homologous series was suggested. The samples analyzed with the Apiezon L-Carbowax 20M reverse column set confirmed the presence of the n-aldehydes, which were prominent features of the primary column Apiezon L chromatogram. Later studies on Chromosorb 102 collected samples, which more accurately presented exhaust species in their actual relative concentrations, showed that the Apiezon L fluidized bed collected a larger relative concentration of aldehydic species. Since the Apiezon L phase is a partition coefficient-dependent sampling medium, species with more favorable partition coefficients are more effectively collected. Although present in the exhaust, some of these aldehydic species were determined to be odor irrelevant from the Chromosorb 102 sample analyses. Among the odorous aldehydes, positive identification of ethanal through octanal in n-aldehyde series was obtained from mass spectral data.

The majority of exhaust and fuel related odors comprising the designations "burnt", "pungent", and "diesel" occurred above Kovats Index 1200 on Carbowax 20M. The odorous Apiezon L components of these peaks appeared at low retention times, indicating polar species. For many of the strong burnt odor peaks, no odorous Apiezon L components could be found. The larger exhaust samples later collected on the high capacity Chromosorb 102 samplers brought these species up to detectable concentrations. The two "foul" components at Kovats Index 1169 and 1269,

on Table VIII, constituted another example of strong odor contribution from low odor threshold species present in small concentrations.

The diesel exhaust samples analyzed with the reverse column set, Apiezon L-Carbowax 20M, were of interest principally for the odor notes from the Apiezon L chromatograms compared with the Carbowax 20M chromatograms. A summary of the odorous peaks is presented in Table IX. The aldehydic notes confirmed the data from the other column set. Above Kovats Index 1200, which represents the end of the temperature program, the Apiezon L column effluent has a continuous background odor that made peak odor annotations difficult. The background odor, whether from the Apiezon L phase or from diffuse sample peaks, could be described generally as "burnt pungent."

C. Chromatographic and Mass Spectrometric Analyses of Diesel Exhaust Samples Collected on Chromosorb 102

The use of the small diameter Chromosorb 102 packed bed samplers, which will completely extract almost all the organic components from the exhaust except for the very light species, permitted the evaluation of odor relevancy of the gas chromatographically separated components. As described in section II-F, a 10 liter sample of diluted exhaust (0.9 liter exhaust) presents the components at the gas chromatograph sniffing port at a concentration about five times the concentration in the actual exhaust. The odor annotations and two-column data from the fluidized bed samples were correlated with the Chromosorb 102 samples. Because of the complexity of the sample and the multi-component nature of the peaks, the shape of the Carbowax 20M chromatograms from the two types of collected samples, of course, differed. However, individual components occurred at the same Kovats Index area.

The mass spectrometric analysis of peaks trapped in the interface unit from the Apiezon L column of the two-column

Table IX

SUMMARY OF ALL ODOROUS PEAKS ON PRIMARY COLUMN APIEZON L CHROMATOGRAM
DUAL-COLUMN CHROMATOGRAPH

Kovats Index Apiezon L	Odor Note
463	sweet
500*	pleasant
544	sweaty
574*	sweaty aldehyde
583	"foul"
630	sweaty aldehyde, "foul"
672*	sweaty aldehyde
724	odor
736	plastic
742	aldehyde
756	unpleasant aldehyde
761	"foul"
774*	aldehyde
785	sweaty, "foul"
800	sharp, aldehyde-burnt
804	pungent-aldehyde
827	sweaty-"foul"
834	aldehyde
837	odor
852	pleasant aldehyde
874*	aldehyde
884	sweaty, "foul"
900	sweaty, "foul"
906	odor
910	odor
911	pungent
918	odor
920	pleasant, minty
931	unpleasant, aldehyde
933	sweaty, "foul"
938	aldehyde
951	unpleasant, "diesel"
958	pleasant, aromatic
962	slight medicinal
975*	aldehyde
980	aldehyde
984	aldehyde
992	sharp aldehyde
1004	aldehyde
1021	medicinal-plastic
1026	aldehyde
1035	pungent
1046	aldehyde
1052	unpleasant burnt
1068	pungent burnt
1076*	pungent aldehyde
1109	sharp pungent, medicinal
1114	pungent burnt
1122	rubber burnt
1134	odor
1138	plastic
1150	odor
1156	unpleasant burnt
1160	burnt pungent
1168	very burnt
1175	burnt
1178*	pungent aldehyde
1189	pungent
1192	unpleasant pungent
1200	odor
ODOROUS PEAKS OCCURRING IN	
1200-1300	KOVATS INDEX RANGE
	sharp burnt
	burnt
	burnt
	pleasant aldehyde*
	burnt pungent
	burnt

*n-aldehyde homologous series, propanal through undecanal.

chromatograph started on fluidized bed collected samples, but samples from the Chromosorb collectors, both 0.375" diameter and high capacity 0.75" diameter packed beds, were used for the major portion of the work.

A typical Carbowax 20M chromatogram from a 100 liter diluted exhaust (9.1 liter exhaust) sample collected on a high capacity Chromosorb 102 sampler is shown in Figure 7 a-g as a reference for the diesel exhaust data summary in Table X. The weight of total organic content for this sample size,[7] obtained by electronic integration of Carbowax 20M peak areas through Kovats Index 1800, was 0.2 mg. Peak No. 5 on Figure 7-a, acetone, was exceptionally large on this particular sample set. It was traced to a leak at the cold trap on the engine sampling system. It does, however, demonstrate the collection capacity of the Chromosorb.

The compilation in Table X, consisting of the odor relevant sample components, lists the two-column data of Carbowax 20M Kovats Index and Apiezon L retention time, odor characterization, concentration estimate, and mass spectral identification or species suggested by the mass spectral data if a positive identification could not be established. No attempt was made to gather complete quantitative information on individual components. The prime consideration was determining whether a component was present in the exhaust above or below its odor threshold, regardless of its absolute concentration. Some concentration estimates are given to show the amounts of different types of species which are odor relevant. The estimates are reliable to within an order of magnitude.

Of the odor relevant species identified, the aromatic hydrocarbons appear to contribute many of the exhaust-related odors. Although toluene, ethylbenzene, and the xylenes are

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[7] The total organic content of the sample is not the total organic content of the exhaust. As explained in section II-B, the sampler does not efficiently collect the very light hydrocarbons, methane for example, which are assumed to be odor irrelevant.

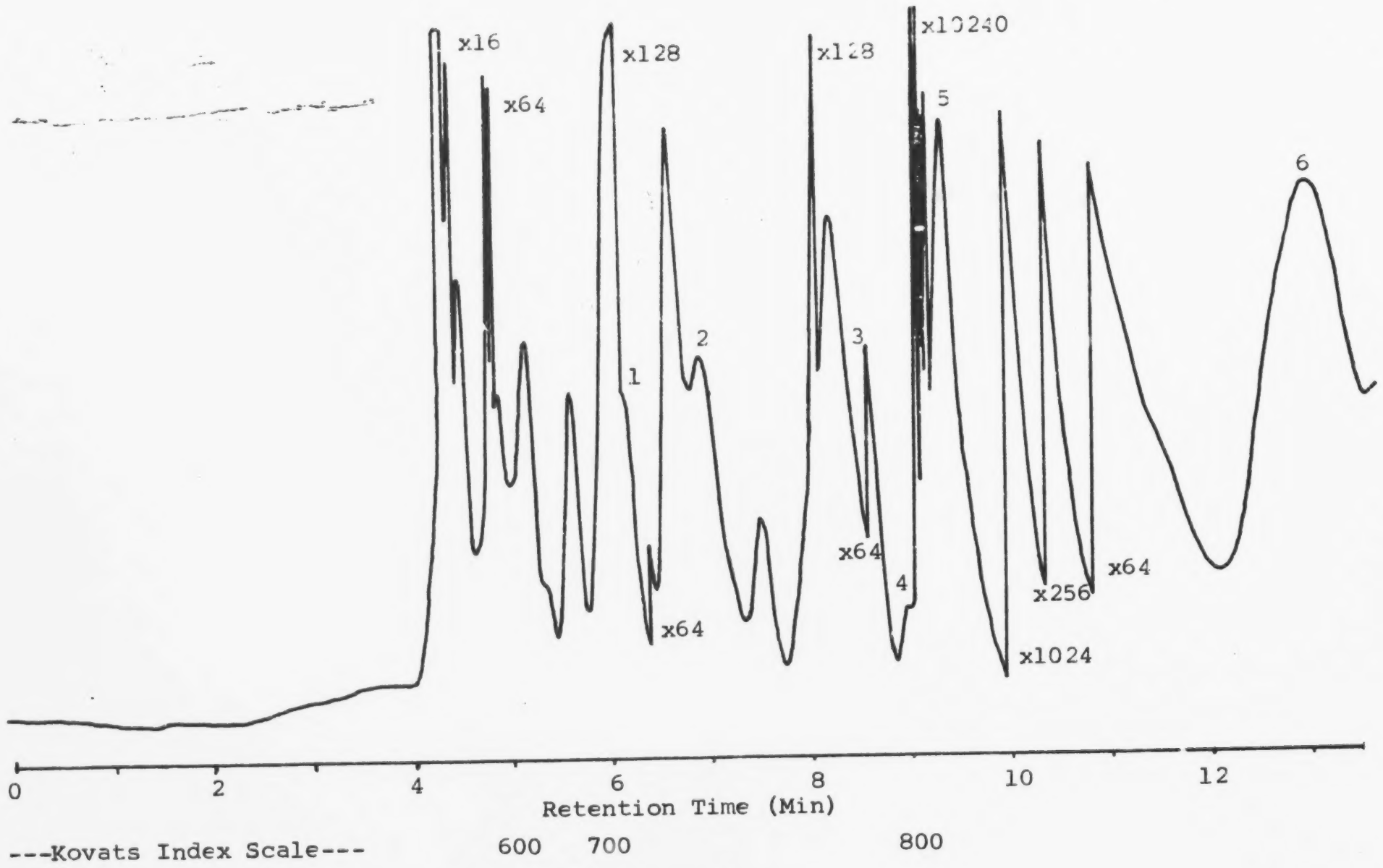


Figure 7 a

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

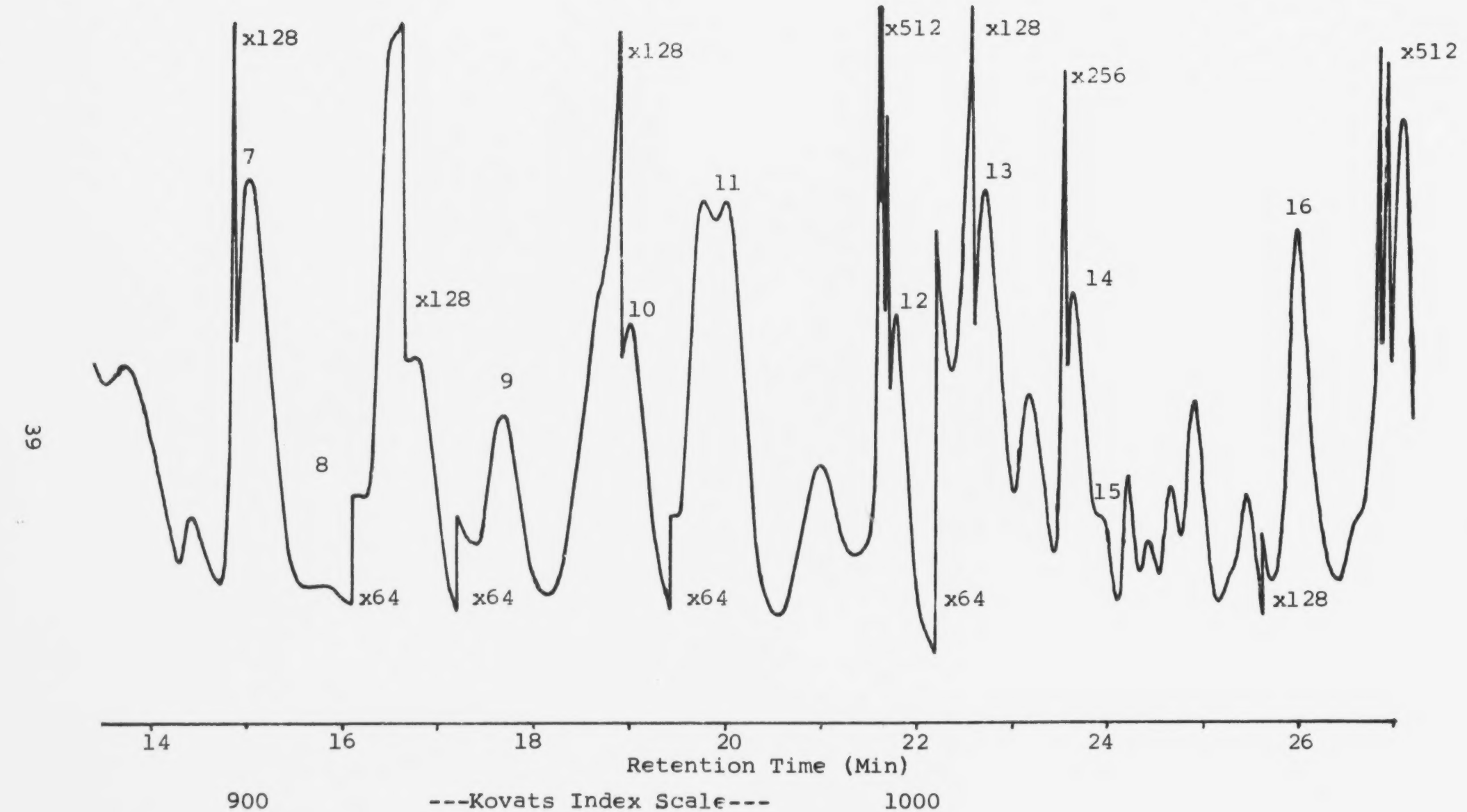


Figure 7 b

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

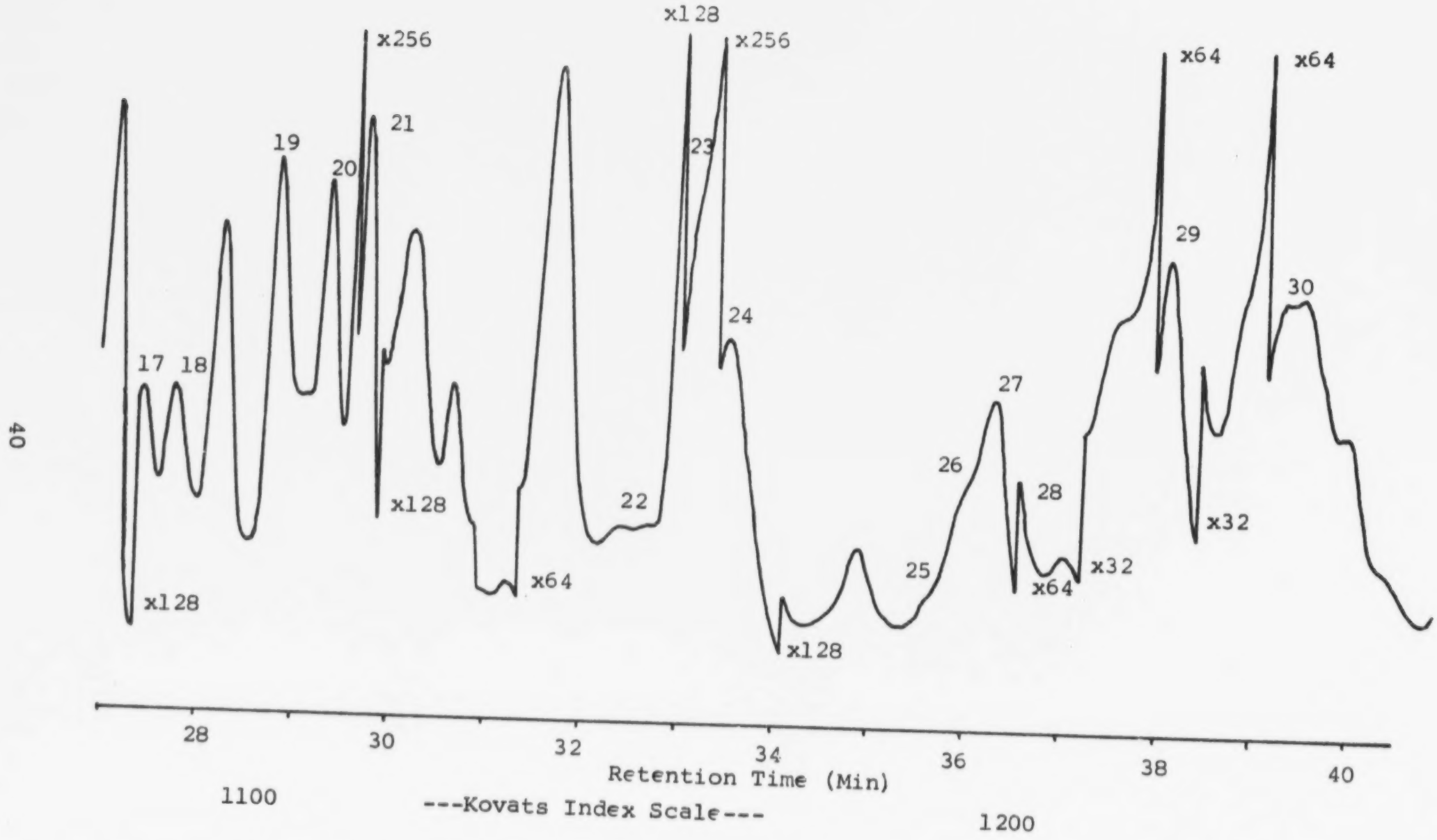


Figure 7 c

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

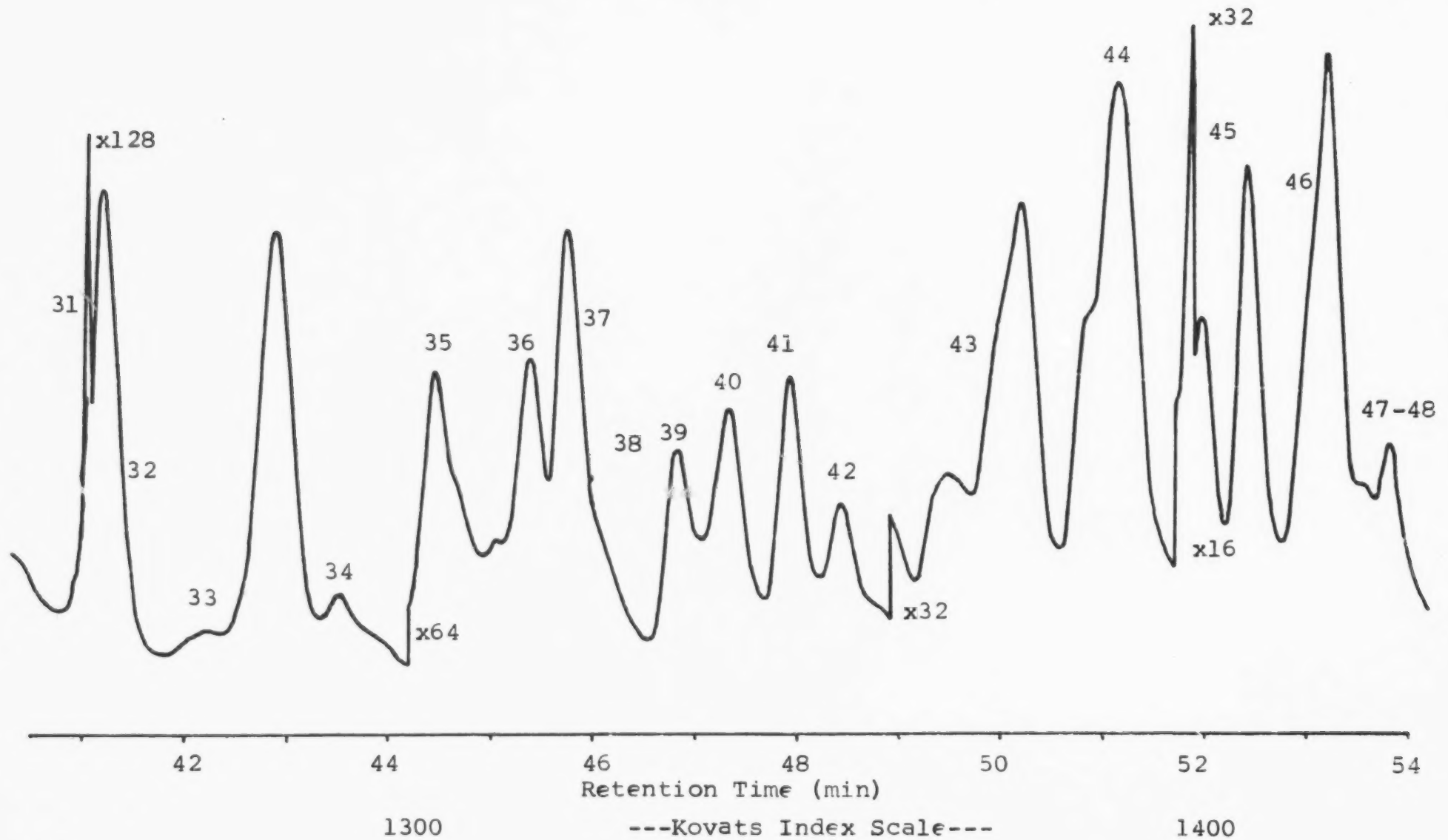


Figure 7 d

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

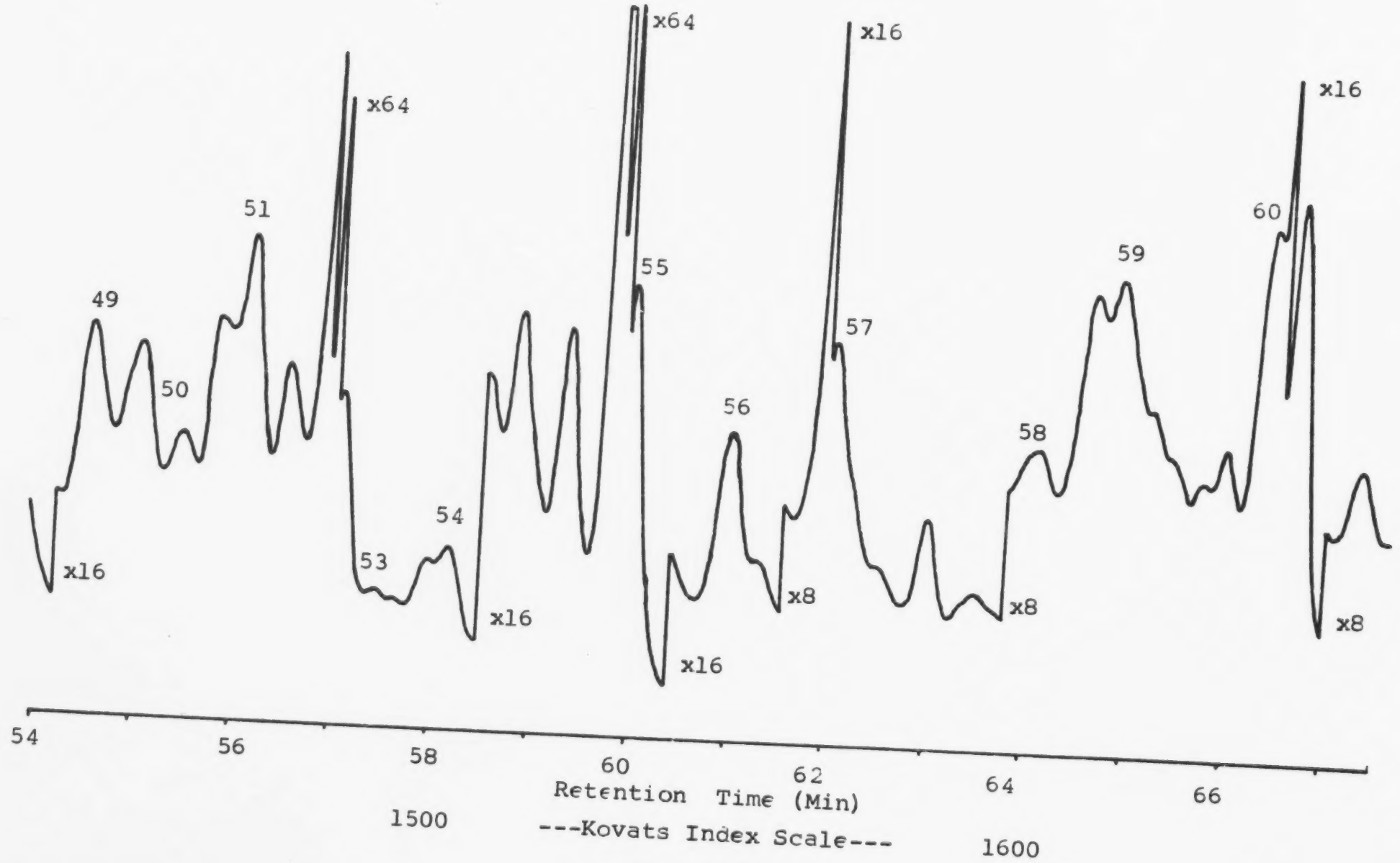


Figure 7 e

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

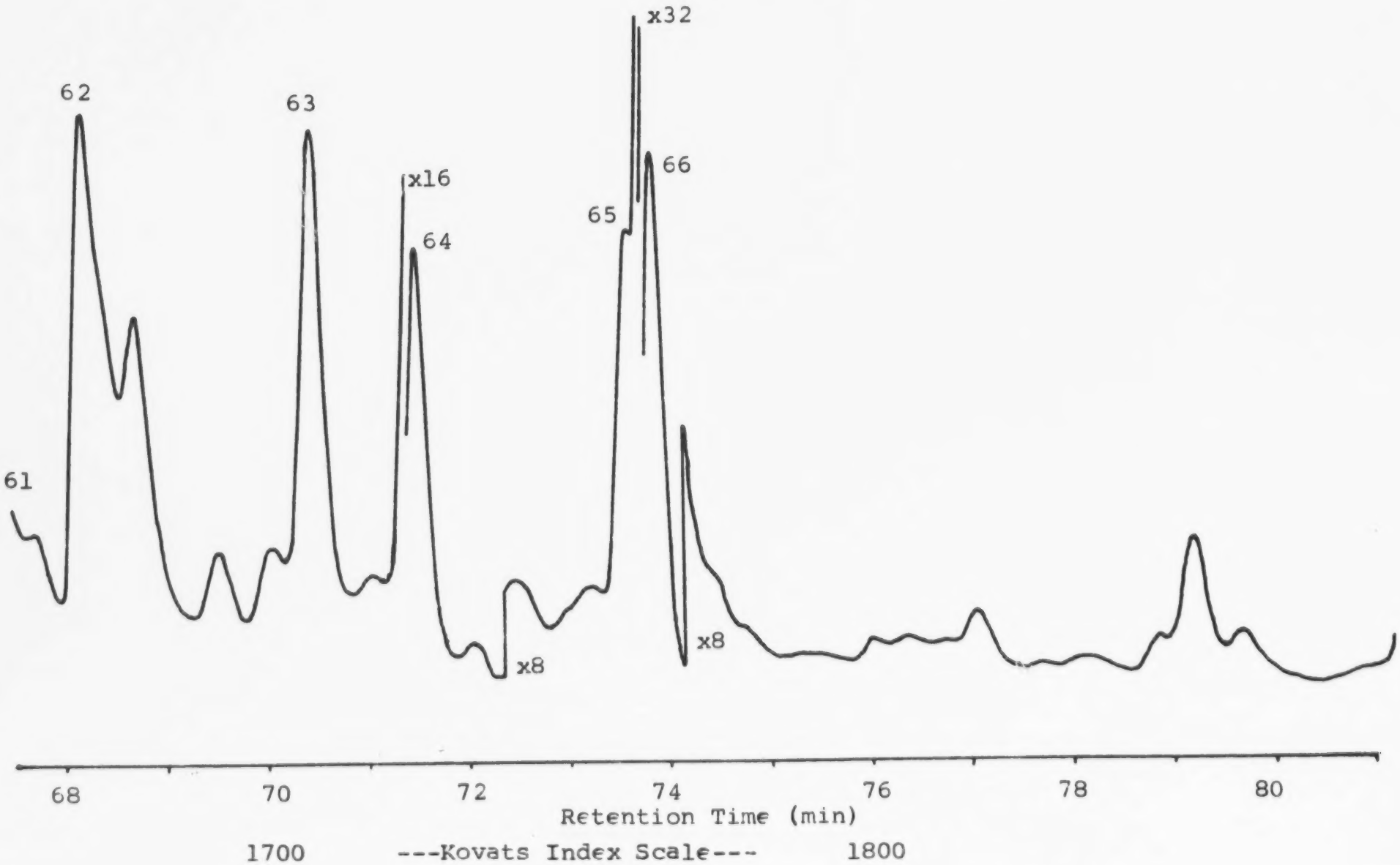


Figure 7 f

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

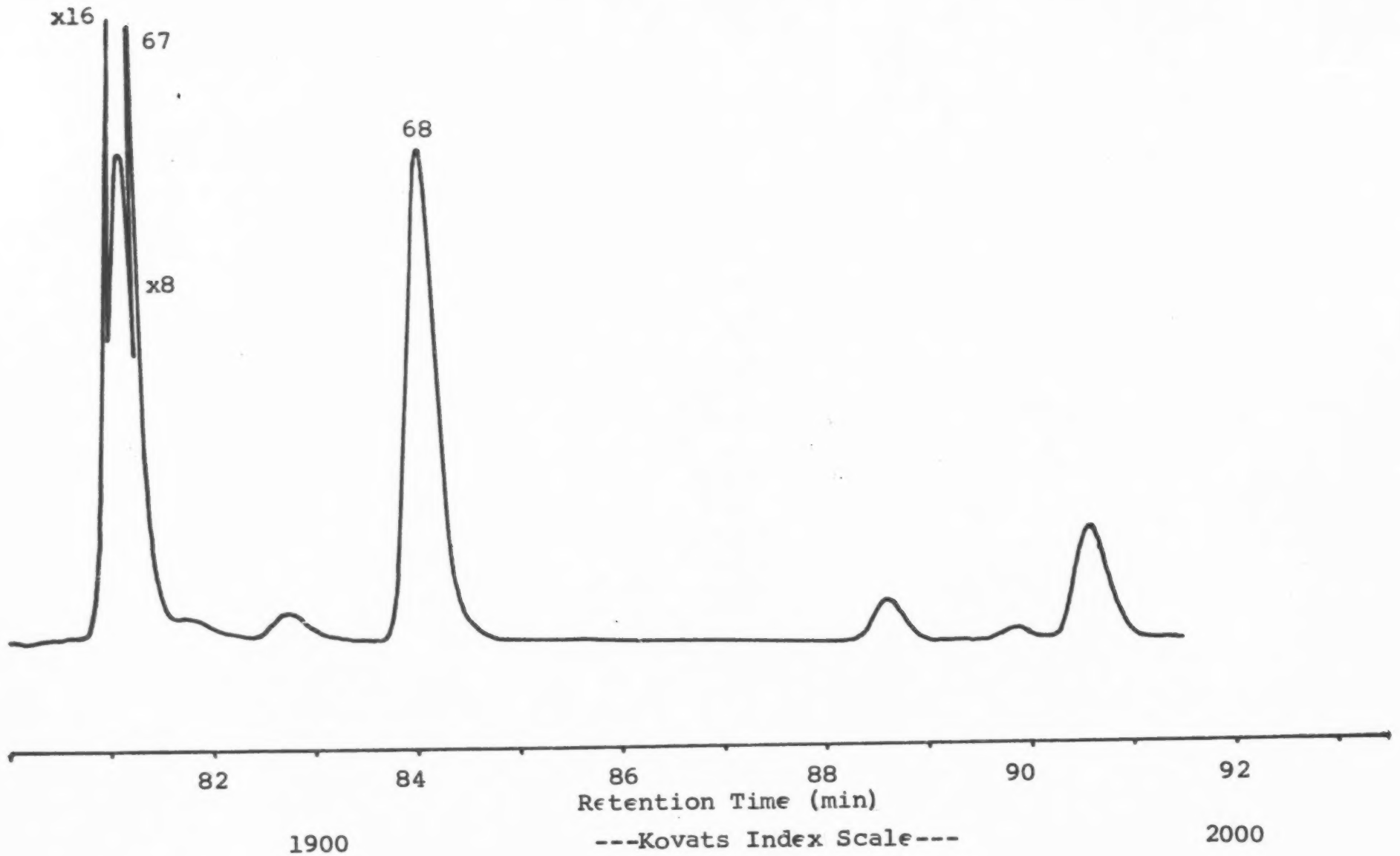


Figure 7 g

CARBOWAX 20M CHROMATOGRAM OF DIESEL EXHAUST COLLECTED ON A HIGH CAPACITY CHROMOSORB 102 SAMPLER

Table X

DATA SUMMARY ON ODOR RELEVANT EXHAUST COMPONENTS

Peak No.[a]	Kovat Index Carbowax 20M	Retention[b] Time Apiezon L (min)	Odor Notes	Exhaust Concn. 10^{-9} g/l	Mass Spectral Data
1	710	0.3	sweet	0.06	ethanal
2	723	0.3-0.5	sweet	0.3	
3	788	0.3	sweet		n-propanal
4	800	0.5	foul		
5	809	0.3-0.5	pleasant		acetone
6	869	0.5-0.7	unpleasant aldehyde	0.5	n-butanal
7	895	0.3	pleasant		2-propanol
8	913	1.0	foul	0.2	
9	934	0.6	foul		
10	957	0.5	strong foul	0.1	possibly acetoin, methylallylketone, and 1,2,3,4-diepoxybutane
11	973	0.8	unpleasant aldehyde		n-pentanal
12	1000	8.9	(non-odorous)	2×10^{1}	decane
13	1015		aldehyde		
14	1031	1.7	(non-odorous)		toluene
15	1035	1.4	unpleasant aldehyde		
16	1069	1.2	aldehyde		n-hexanal
17	1091	1.0-1.3	pungent aldehyde		
18	1093	1.2	unpleasant burnt	0.02	possibly cyclic olefin or alkyne
		1.4	pungent burnt		
19	1109	1.0	pungent plastic		
		2.2	pungent		ethylbenzene
20	1118	2.3	pungent		p-Xylene
		2.6	pungent burnt	1	possibly 1,7-octadiyne
21	1126	1.8	pungent-fruity-aldehyde		
		2.3	pungent		m-Xylene
22	1162	2.6	burnt-pungent-"garage"	0.6	hydrocarbon with 2 positions of unsaturation
23	1169	1.2	foul	0.02	
24	1171	1.4	aldehyde, citrus		n-heptanal
25	1191		pungent		
26	1195	1.4	aldehyde		
27	1200	2.0	burnt	0.002	
28	1205	2.9	pungent		
29	1216	3.85	strong burnt	0.004	
30	1230	1.5	burnt		
	1230-50		burnt, pungent, aldehyde odors		
31	1269	1.6	strong foul		trimethylthiophene
32	1273	3.4	pungent, fuel		C_4 substituted benzene
33	1279	1.7	aldehyde		n-octanal
		2.7	pungent		trimethyl- or methyl-ethyl-benzene
34	1292	1.4	unpleasant burnt	0.05	methallylbenzene (2-methyl-3-phenyl-1-propene) or p-ethyl styrene
	1294	1.6	strong burnt	0.005	
35	1300	1.0	unpleasant		
		1.4	pungent-burnt	0.1	
		2.9	pungent-burnt	0.2	
36	1310		pungent aldehyde		
37	1319		burnt acrid		
38	1329	1.8	unpleasant	0.01	
		4.3	strong unpleasant burnt	0.004	
39	1332	3.2	pungent burnt	0.2	C_5 substituted benzene

Table X (cont.)

Peak No.[a]	Kovats Index Carbowax 20M	Retention[b] Time Apiezon L (min)	Odor Notes	Exhaust Concn. 10^{-9} g/l	Mass Spectral Data
40	1340		burnt		
41	1347		pungent aldehyde		
42	1358		burnt pungent		
43	1384	2.1	pungent, aldehyde		C_4 substituted benzene and probably nonanal
44	1392	1.5	unpleasant burnt		
45	1400	3.4	pungent burnt		possibly substituted cyclohexane and substituted cyclohexene
46	1422		burnt pungent		
47	1432	1.5	burnt pungent	0.02-0.2	allyltoluene
		2.0	burnt	0.002	
		2.7	burnt pungent		C_4 substituted benzene
48	1433	1.8	pleasant pungent		
49	1442	3.3	fragrant, floral	0.3	
50	1455		pungent burnt		
51	1466	1.1	unpleasant burnt	0.006	
		3.1	strong burnt	0.2	substituted cyclohexane and probably sulfur species
52	1470	0.6	pungent		furaldehyde
53	1491	2.4	pungent aldehyde		alkylbenzene and probably decanal
54	1500	3.2	burnt-fuel	0.4	methylindan
55	1535	0.8	cherry pungent	1.5	benzaldehyde
		2.1	burnt	0.01	
		3.3	burnt	0.1	C_5 substituted benzene and C_2 substituted benzothiophene
56	1555	4.3	pungent		
57	1569	3.1	strong burnt pungent	0.5	ethyl- or dimethylcumene
		3.4	unpleasant burnt		
58	1600	2.7	pungent aldehyde		
59	1625	3.2	burnt-fuel		dimethylindan
60	1639	3.1	burnt	0.2	
61	1661	1.1	unpleasant burnt		
		3.9	burnt rubber	0.05	methyltetralin
62	1666	0.9	pleasant, floral		tolualdehyde and acetophenone
63	1707	3.2	pungent burnt	0.1	C_5 substituted benzene
64	1722	1.2	pleasant, sweet		methylacetophenone and C_2 substituted benzaldehyde
65	1758	2.0	sweet, floral		ethylbenzaldehyde
66	1764	2.0	naphthalene	2	naphthalene
67	1871	3.3	naphthalene	2	methylnaphthalene
68	1909	3.7	naphthalene		methylnaphthalene

[a] Peak number refers to Figure 7a-g.

[b] Retention time in the Apiezon L column is corrected for column dead volume.

borderline cases of odor relevancy, the higher substituted benzenes, indans, and tetralins are present in odor relevant concentrations. High odor intensity was also characteristic of the naphthalenes and aldehydes identified and particularly the aldehyde and ketone derivatives of benzene, but these individual odor qualities are submerged in the total exhaust odor. The series of odor-important components characterized as "foul" were not all identified, but the data obtained suggest that several different low threshold types may contribute this type of odor, including oxygenates, highly unsaturated hydrocarbons, and sulfur species.

Some burnt odor qualities can be attributed to the aromatic species and unsaturated aliphatics, but there are also several very strong burnt odor species with exceptionally low thresholds. These species occurred at Kovats Indexes ~1200, 1216, ~1294, 1329, and 1432. During earlier investigations, no odorous components could be found on the Apiezon L chromatograms from these Carbowax 20M peaks. The larger samples taken on the high-capacity Chromosorb collectors increased the component concentrations to the amount necessary to produce a detectable peak on the Apiezon L chromatograms to signal for odor monitoring. Figures 8a and 8b show sections of the Apiezon L chromatograms produced by four of these strong burnt Carbowax 20M peaks. The area on the chromatogram producing the same odor quality and intensity is designated. The very small concentrations involved precluded any mass spectrometric investigations of these species.

Correlations between the gas-chromatographic positions in the two-column chromatograms and the physicochemical and functional characteristics of the compounds (Figure 1 and Appendix G) permit inferences on some properties of these unidentified burnt-odor components. Thus, approximate boiling

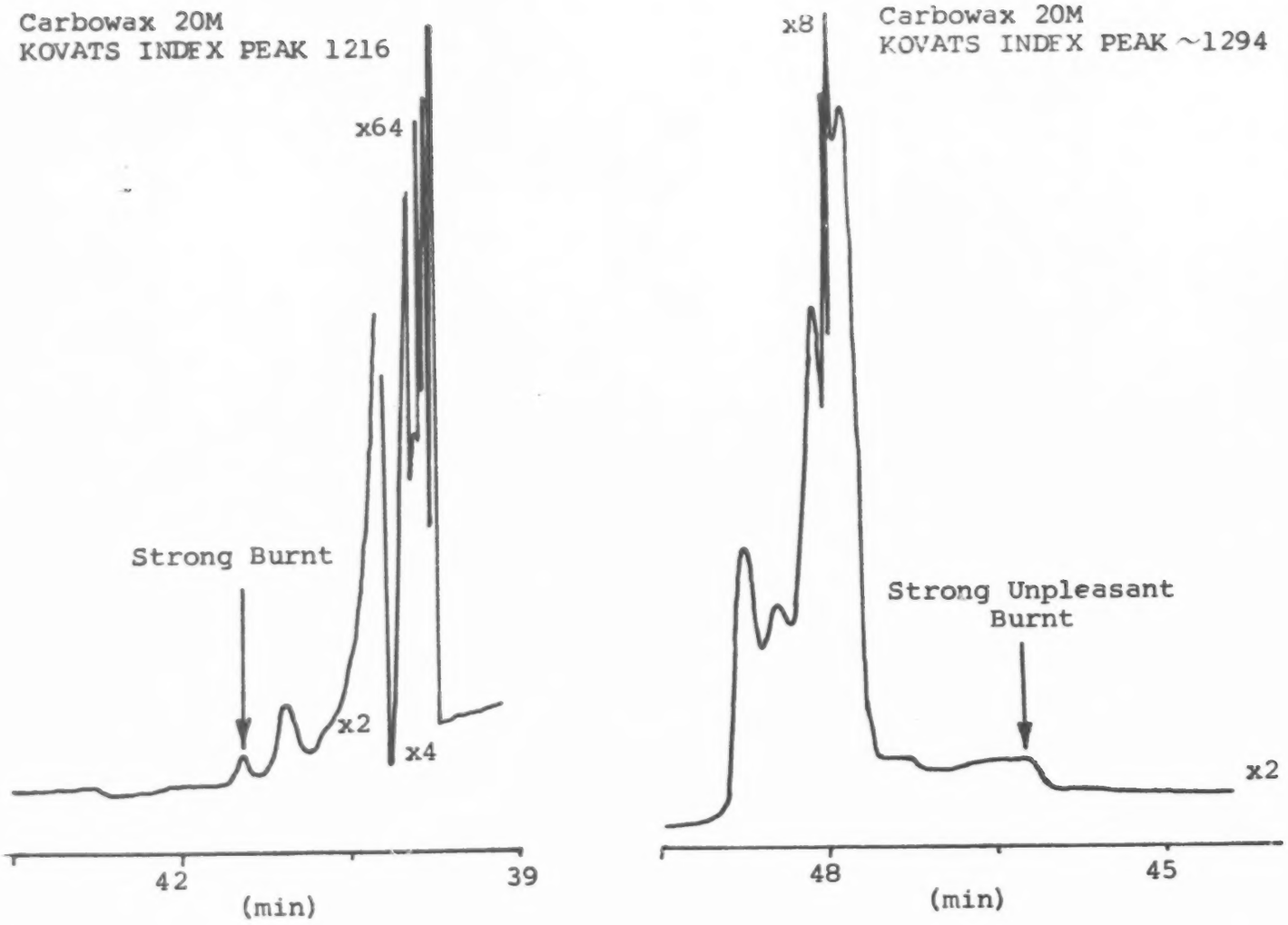


Figure 8 a

APIEZON L CHROMATOGRAMS OF STRONG BURNT CARBOWAX 20M PEAKS

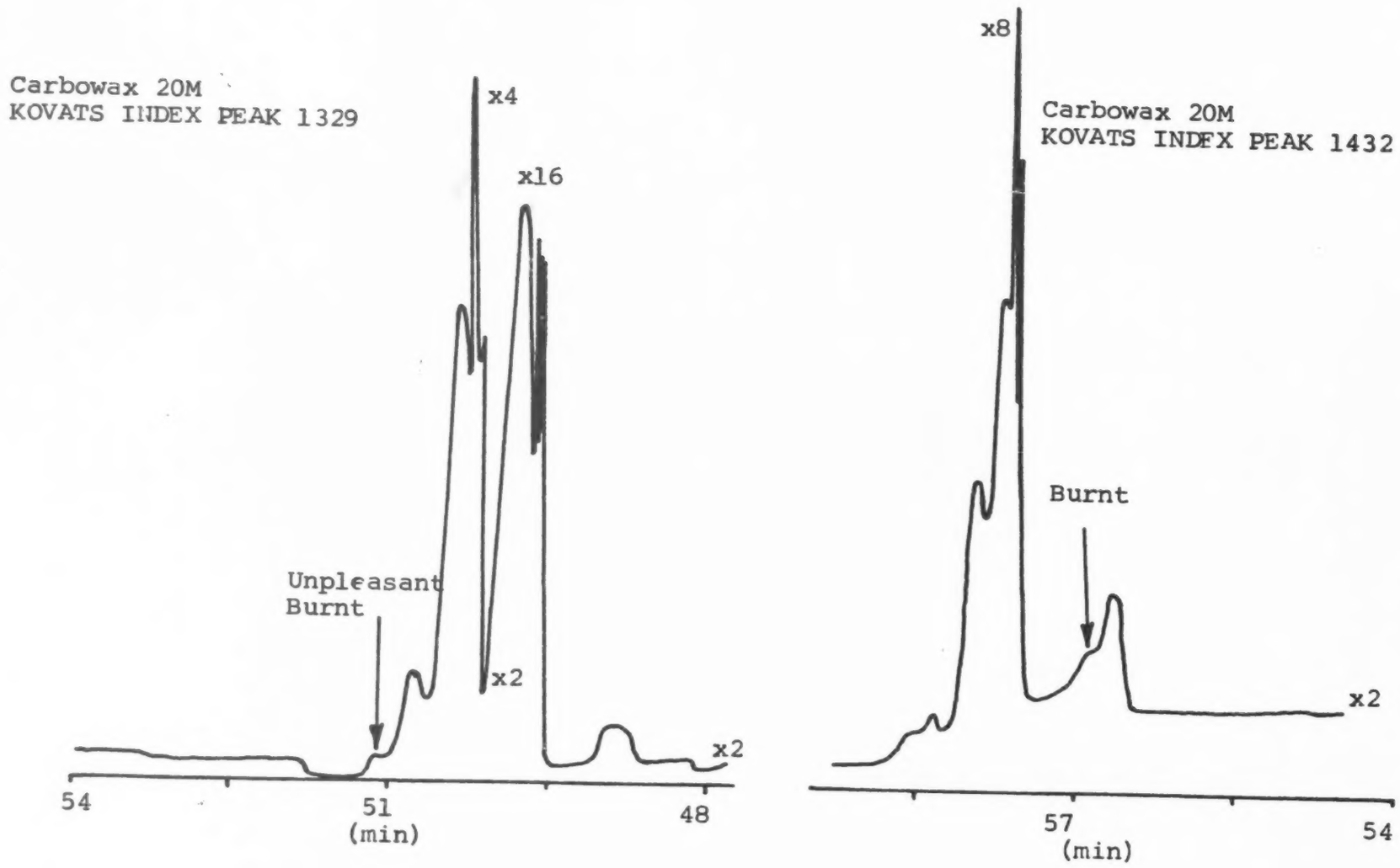


Figure 8 b

APIEZON L CHROMATOGRAMS OF STRONG BURNT CARBOWAX 20M PEAKS

points, °C, and molecular weights of the five mentioned burnt components are estimated: 165°, 130; 190°, 170; 170°, 130; 210°, 150; and 200°, 155, respectively. The presence of -OH group is excluded. The Kovats Index 1216 and 1329 components are relatively nonpolar and cannot be simple aldehydes, other carbonyl compounds, aryls, or derivatives of cyclic ethers. The degree of polarity also excludes non-cyclic alkenes, but cyclic olefins are possible. The Kovats Indexes 1200, 1294, and 1432 components have polarity of the order of saturated carbonyl compounds, including branched aldehydes or aromatic derivatives without heteroatoms but with additional unsaturation in the side chain.

D. Acidic and Phenolic Components in Diesel Exhaust

Because acidic and phenolic compounds do not chromatograph on the Carbowax 20M column, diesel exhaust samples were analyzed on a packed column of Chromosorb 101 to specifically determine the presence and odor relevance of these species in the exhaust. Several acidic and phenolic standards were run on the column to obtain retention data and odor references. The diesel samples analyzed were poorly resolved, but emphasis was placed on the odor analysis of the column effluent since the compound types sought would elute as distinct, though perhaps unresolved, peaks.

Figure 9 presents a summary of the calibration data and the relevant odors from the exhaust chromatograms in Kovats Index notation. Definite acidic odors were recognized at retention times characteristic of 2-through 6-carbon acids with the most intense odor for a C_5 acid. To provide some basis for comparison with other chromatographic odor annotations, the acidic odor intensities can be said to be comparable to the aldehyde odors in the same effluent.

A definite conclusion on the presence of phenolic compounds in the exhaust was difficult to make from the data obtained. In

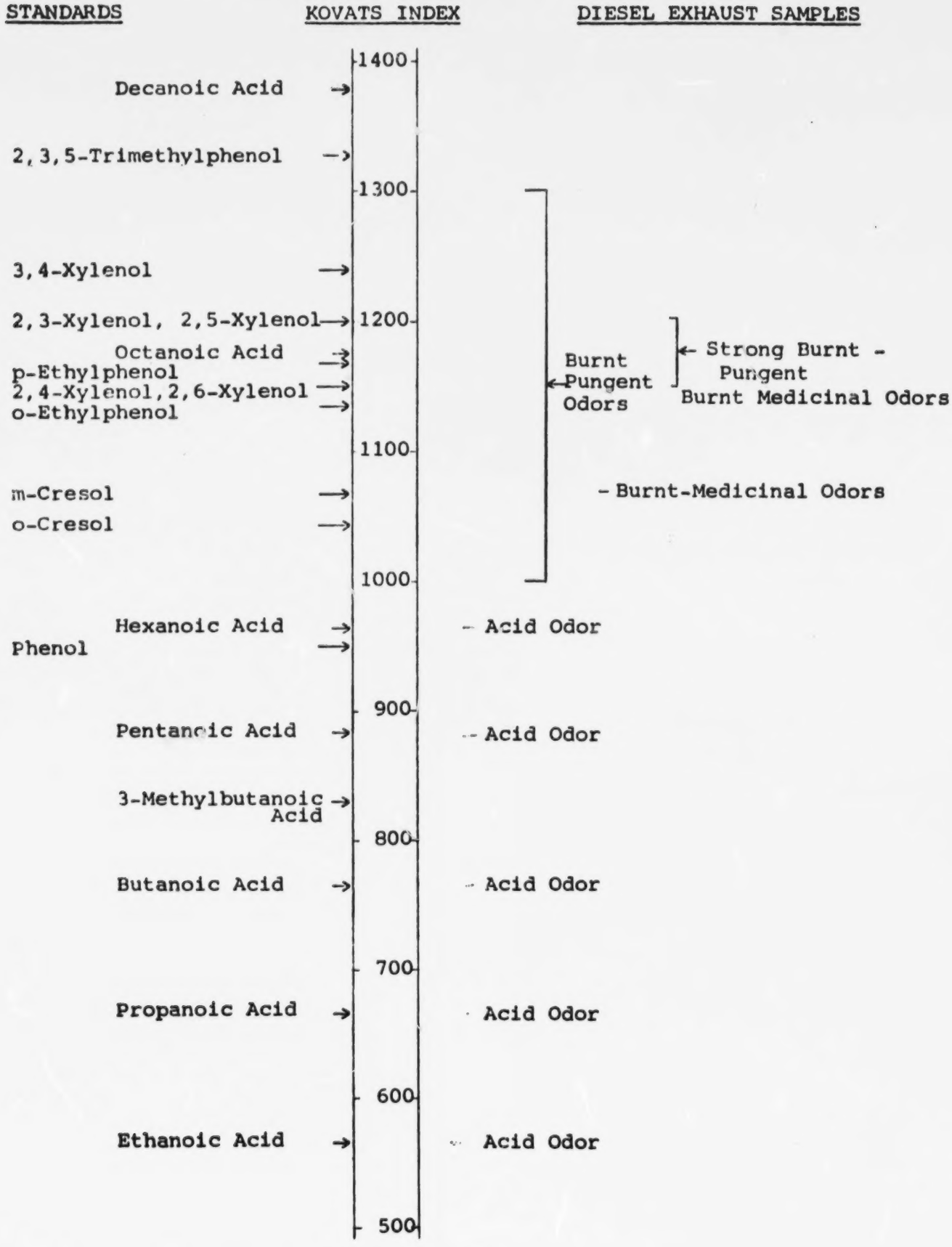

STANDARDS
KOVATS INDEX
DIESEL EXHAUST SAMPLES
1400
Decanoic Acid
2,3,5-Trimethylphenol
1300
3,4-Xylenol
2,3-Xylenol, 2,5-Xylenol
1200
Octanoic Acid
p-Ethylphenol
2,4-Xylenol, 2,6-Xylenol
o-Ethylphenol
Burnt Pungent Odors
Strong Burnt - Pungent Burnt Medicinal Odors
1100
m-Cresol
o-Cresol
- Burnt-Medicinal Odors
1000
Hexanoic Acid
Phenol
- Acid Odor
900
Pentanoic Acid
- Acid Odor
3-Methylbutanoic Acid
800
Butanoic Acid
- Acid Odor
700
Propanoic Acid
- Acid Odor
600
Ethanoic Acid
- Acid Odor
500

Figure 9

the retention time areas of phenolic compounds the column effluent odors were best described as burnt-pungent. In some instances there was a sweet or pleasant overtone, and the presence of a slight medicinal-type odor was occasionally detected.

Appendix A

EMISSION SOURCE AND SAMPLING APPARATUS

Appendix A

EMISSION SOURCE AND SAMPLING APPARATUS

The exhaust sampling system is presented in Figure A-1. The diluent nitrogen is first rendered non-odorous by passage through an activated charcoal filter immersed in a dry ice-acetone bath. It flows through an air coil, where it is warmed to about 50°F, and then through a jet syphon (Schutte and Koering type 217 steam syphon) where it dilutes and cools a portion of the engine exhaust. The diluted mixture travels into a plenum chamber where some is collected by the sampling devices. The major portion of the engine exhaust is discharged, undiluted, from the engine laboratory. Generally, the volume of engine exhaust diverted into the sampling stream was 0.3 scfm, and the volume of nitrogen diluent used was 3.2 scfm.

The entire system is fabricated from stainless steel, glass, or Teflon, with the exception of the plenum. The plastic plenum is lined with a polyethylene bag which is replaced each time the engine exhaust is sampled. The volumes of extracted exhaust and diluent nitrogen are measured with calibrated sharp-edged orifice plate meters. Temperatures are measured with either chromel-alumel thermocouples or bimetallic thermometers. Engine operating conditions during exhaust sampling are compiled in Table A-I.

Mobil Research and Development Corporation supplied the data on their #1 Diesel Fuel presented in Table A-II.

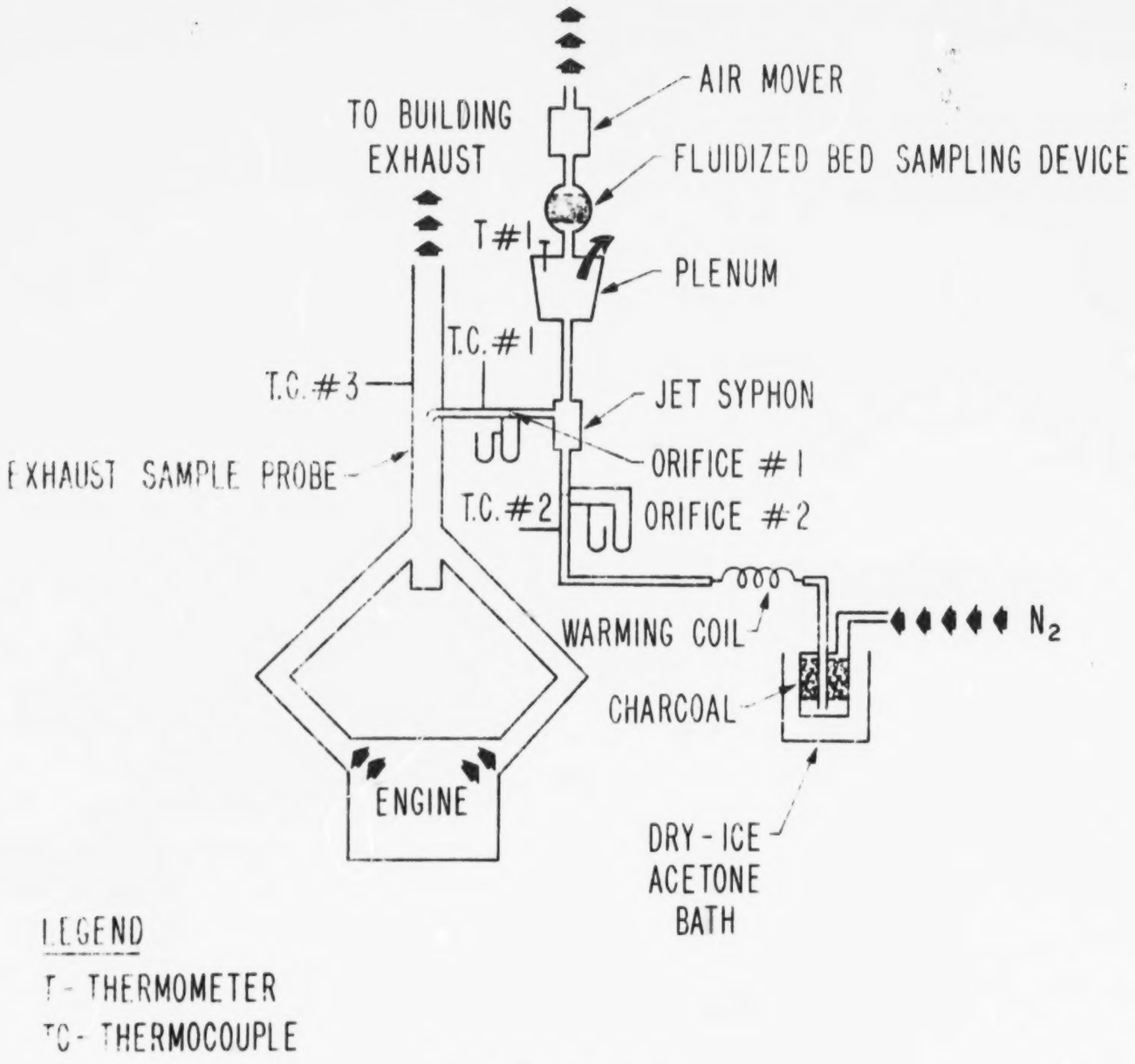


Figure A-I

DIESEL EXHAUST SAMPLING SCHEME

Table A-I

ENGINE OPERATING AND SAMPLING CONDITIONS
Detroit V-71 Diesel Engine

Parameter	Typical	Range
Engine speed rpm	1200	1200 -1250
Engine load, ft-lb	134	131 - 134
Engine horsepower	54	52 - 54
Engine cooling water temperature, °F	188	180 - 190
Fuel flow, lbs/hr	25	21 - 26
Fuel pressure, psig	30	23 - 37
Oil pressure, psig	55	47 - 57
Air intake flow scfm	340	322 - 382
Exhaust temperature, °F, T.C.#3	450	420 - 480
Room temperature, °F	78	77 - 89
Room humidity, %RH	23	22 - 33
Room pressure in. Hg	29.2	28.4 - 29.9
Exhaust sample line temperature °F, T.C.#1	120	110 - 132
Nitrogen sample line temperature °F, T.C.#2	50	45 - 70
Diluted nitrogen-exhaust sample T#1	80	77 - 85

Table A-II

ANALYSIS OF DIESEL FUEL[1]

Test		Analysis
Gravity, API		42.4
Distillation, °F -	Initial	354
	10%	398
	50%	459
	90%	534
	End	580
Flash Point, °F		150
Aniline Point, °F		151
Sulfur, % wgt		0.13
Total Mercaptan, ppm, wgt		< 0.5
Mercaptan, NaOH Extract, ppm, wgt		< 0.5
Viscosity, Centistokes @ 100°F		1.89
FIA Analysis, % by volume		
	Aromatics	15.3
	Olefins	1.7
	Saturates	83.0
Cetane Index		55.5
Cetane Number		56
Nitrogen, ppm		14
Color, L		0.5
Phenols, ppm		149
Thiophenols, ppm		9

[1]Mobil #1 Diesel Fuel.

Appendix B

EXHAUST SAMPLING DEVICES

Appendix B

EXHAUST SAMPLING DEVICES

The fluidized bed sampler, shown in Figure B-1, is a glass column, 5 in. x 1.25 in. diameter, containing 10 g of 40/60 mesh Fluoropak 80 with a 15% Apiezon L coating. Stainless steel screens at each end of the column hold the loose packing medium in the chamber. A small blower pulled the diluted diesel exhaust through the bed at a rate of 45 liters per min. The exhaust was sampled for a period of 30 min, permitting about 125 liters of undiluted exhaust to pass through the collector. Generally, eight fluidized bed samples were collected from each engine run.

The packed bed samplers are stainless steel tubes, 10 in. x 0.375 in. diameter, with 0.125 in. o.d. stainless steel tubing silver brazed to the ends. The collector holds 4.2 g of the collection phase, either 15% methylsilicone SF-96 on 80/100 mesh Chromosorb HP or the solid adsorbent C-102 in 60/80 mesh size. During exhaust sampling, the bed was connected through a dry ice-acetone cold trap to a leveling bulb containing silicone oil, and 2 liters of the dilute exhaust were pulled through the bed by displacement at a rate of 100 ml/min.

To collect larger samples and to take advantage of the faster collection rate possible with the C-102 material, a wider diameter packed bed sampler was fabricated. The collector design is shown in Figure B-2. It consists of a 0.75 in. o.d. thin-wall stainless steel cylinder, 4 in. long with 0.125 in. o.d. stainless steel tubing ends. The packing material, 5 g of 60/80 mesh C-102, is held in place by two 100 mesh stainless steel screens, one fixed and the other spring loaded to provide reasonable compaction and eliminate channel formation. Diluted exhaust was pulled through these samplers

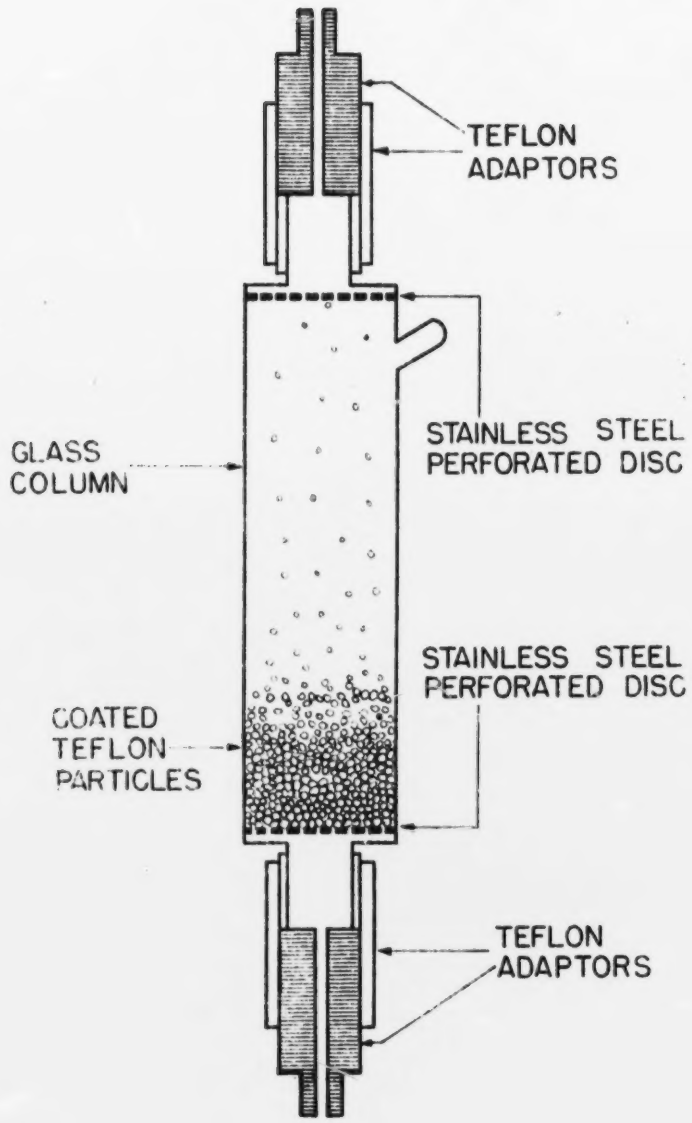
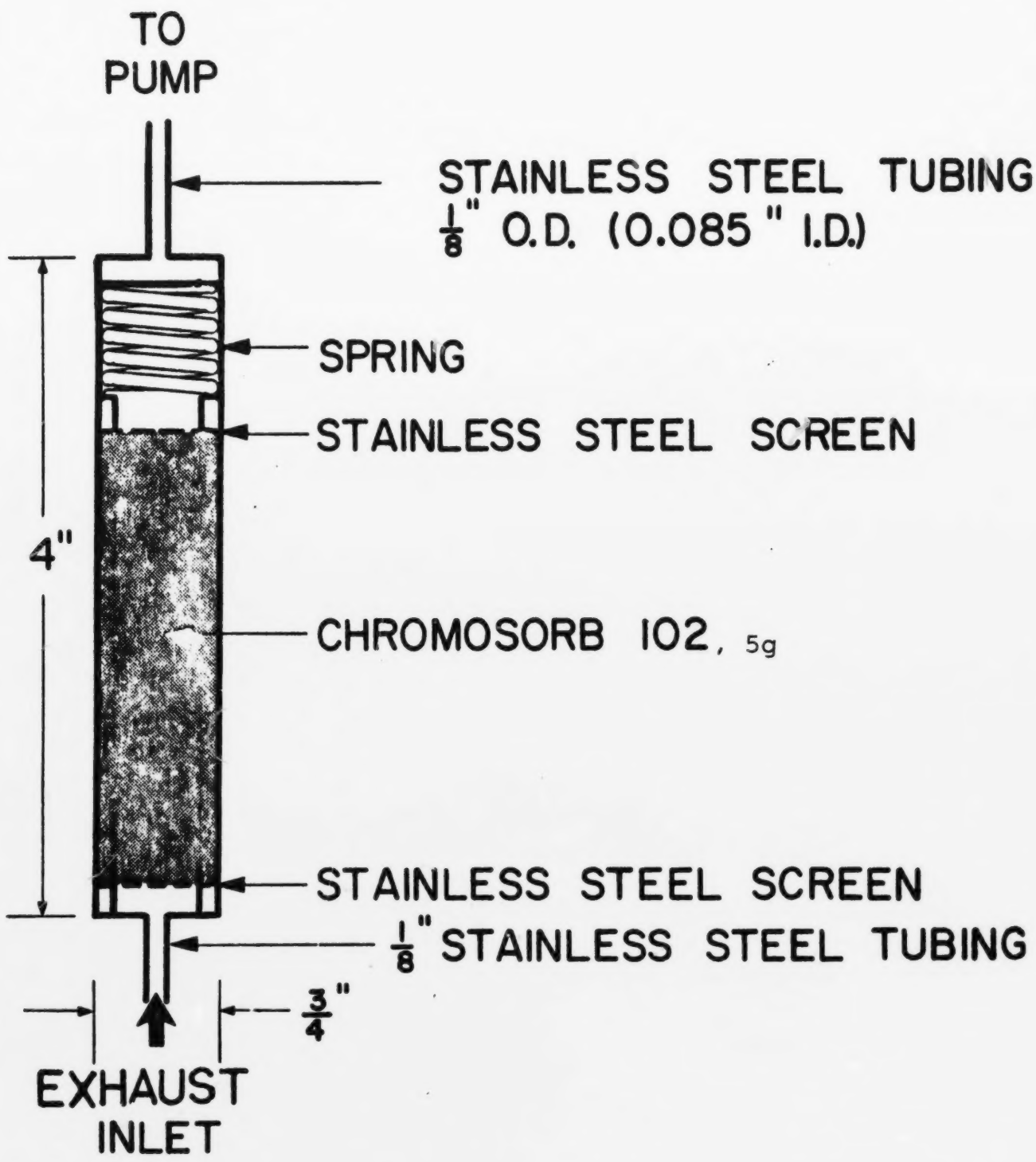


Figure B-I
FLUIDIZED BED COLLECTOR



HIGH-SPEED VAPOR COLLECTOR

Figure B-2
HIGH-SPEED ORGANIC VAPOR COLLECTOR

at a rate of 3 liters/min for a total sample of 100 liters (9.1 liters of undiluted exhaust).

All sampler types were cleaned and conditioned before use by passing a purified helium flow of 60 cc/min through the samplers at elevated temperatures for a minimum period of 18 hr. Conditioning temperatures were determined by the specific temperatures used for elution of collected sample. Conditioning efficiency was checked gas chromatographically with blank elution samples. Teflon tubing was used for connections to the samplers, and the ends were sealed with Teflon plugs.

Appendix C

SAMPLE ELUTION AND INJECTION TECHNIQUES

Appendix C

SAMPLE ELUTION AND INJECTION TECHNIQUES

Samples collected in fluidized or packed beds were transferred to a specially designed needle for introduction into the gas chromatograph using the assembly shown in Figure C-1. The collector is placed in an aluminum block thermostatted at 120°C (80°C for Apiezon L fluidized beds). Zero quality helium is passed first through a liquid nitrogen cooled copper coil, then through the collector (in a direction opposite to the direction of sampling into the collector), and into a stainless steel injector needle at a rate of 60 ml/min. During the transfer of sample, the injector needle is held in a rectangular cross section groove in a liquid-nitrogen-cooled block (shown only schematically in Figure C-1). The groove is covered with a copper plate. A copper rod from the block extends into a Dewar of liquid nitrogen. A copper side tube provides a path for the nitrogen to the cooling groove so that boiling nitrogen in this side tube generates sweep gas which purges the groove volume and prevents the formation of ice around the injector needle. The connection between the collector and injector is made with Teflon tubing. The connections are actually heated up to the larger portion of the injector needle to prevent any condensation of sample before this point. A rotameter connected to the end of the injector needle monitors the helium flow.

The injector needle design is shown in enlarged view in the upper section of Figure C-1. The right end of the injector is inserted into the injection port of the gas chromatograph, and the left end is connected to a bellows mechanism. The restrictor in the left end prevents backflow of sample when the sample is later heated for injection.

After the sample has been transferred to the injector, it is connected to the gas chromatograph through a modified

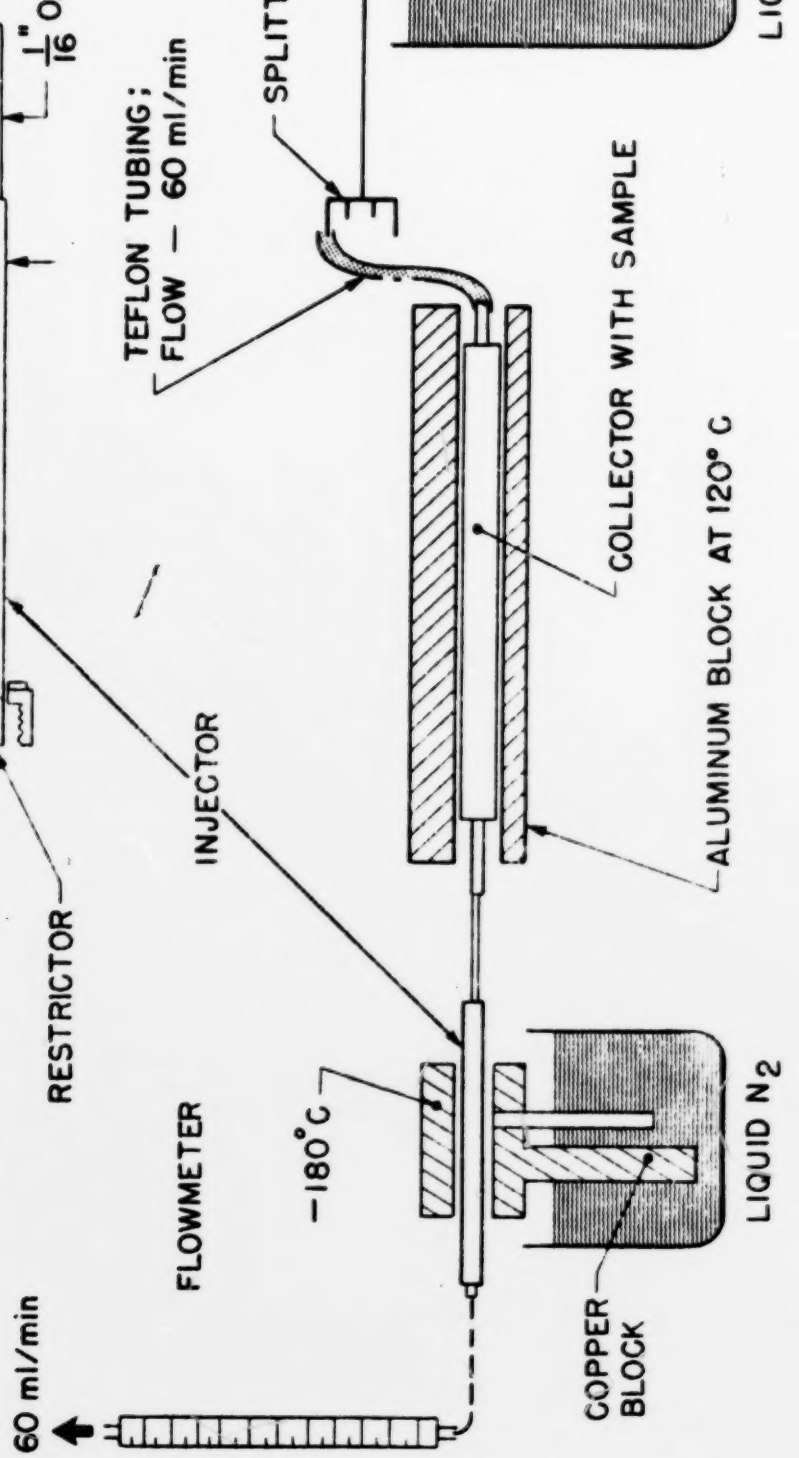


Figure C-1

COLLECTED SAMPLE IS TRANSFERRED TO INJECTOR

injection port that consists of a stainless steel fitting with a Teflon compression plug sealing element.* The plug has a 0.0625" hole through which the small end of the injector is inserted. A seal is produced by tightening the nut surrounding the Teflon plug. The other end of the injector is attached to an injection assembly. The entire apparatus is shown in Figure C-2.

After sample transfer, the cold injector is held between two liquid nitrogen cooled copper blocks, slotted to accomodate the 0.125" o.d. tube. A motorized eccentric cam and bellows mechanism pulls 1 ml of carrier gas helium from the gas chromatograph past the cold sample, and stores the helium in the bellows chamber. To inject the sample, the lever is rotated to remove the cold horizontal copper blocks from the injector and replace them with the vertical set, which are preheated to 250°C. Simultaneously, the bellows movement pushes the stored helium through the vaporizing sample and into the chromatograph. After 10 seconds, when the helium injection is completed, the cold blocks are again clamped around the injector. The pressure gauge on the system is necessary to determine when the pressures in the injection-chromatograph system have stabilized after withdrawing carrier gas for injection. The gauge also serves to detect any leaks in the system. When not attached to the GC, the injection system is continuously flushed with helium through the port shown capped for a sample injection. The U-tube between the bellows and the injector needle is immersed in liquid nitrogen to prevent sample contamination from the bellows system.

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*Conax fitting.

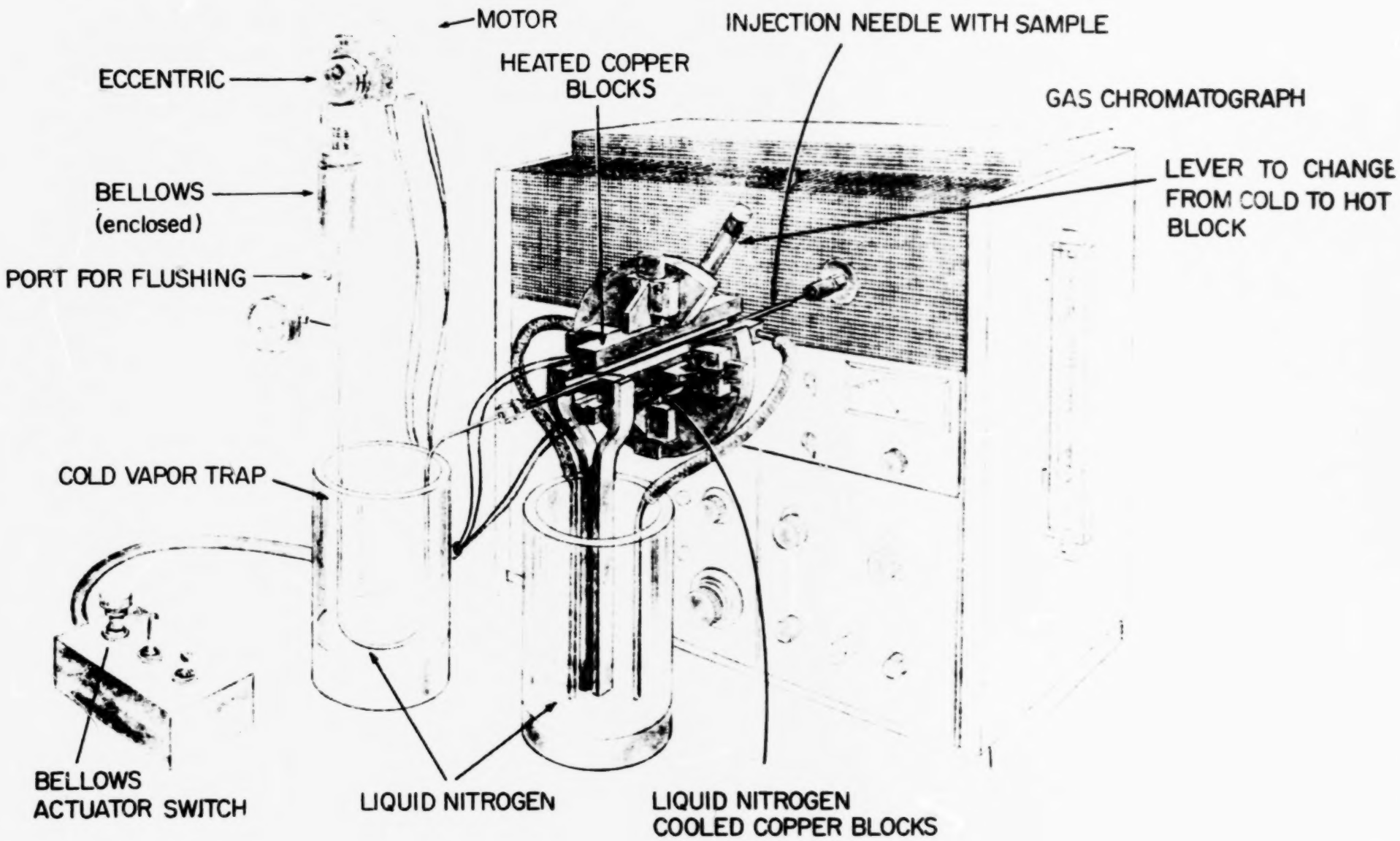

Figure C-2

APPARATUS FOR SAMPLE INJECTION INTO GAS-CHROMATOGRAPH

Appendix D

GAS CHROMATOGRAPHIC EQUIPMENT AND TECHNIQUES

Appendix D

GAS CHROMATOGRAPHIC EQUIPMENT AND TECHNIQUES

The single column chromatograph, an Aerograph Model 1200, is depicted in Figure D-1. Helium carrier gas flows through the column at a rate of 10 ml/min. At the column exit, 30 ml/min of helium is added to the column effluent, and the mixture is split 1:1. One 20 ml/min portion is delivered to the flame ionization detector, and the other half continues to a sniffing port where the odor of effluent peaks is monitored. The two high resolution columns used in the single column instrument were both 200' SCOT columns with an i.d. of 0.020-in. The stationary phases were Apiezon L and Carbowax 20M.

When the packed column, 4' of 3 mm o.d. pyrex tubing, of 60/80 mesh Chromosorb 101 was used, the 40 ml/min column flow provided, after splitting, 20 ml/min flows to both the detector and the sniffing port without the necessity of auxiliary helium. Samples and standards were chromatographed on this column with a programmed temperature rise of 2° or 4°/min from 100° to 300°C.

The sniffing port design is shown in Figure D-2. The portion of the effluent flow for sniffing passes through a Teflon line, maintained at the temperature of the detector, to the outside of the chromatograph housing and into the center of a cylindrical Teflon chimney (2" by 0.75" diameter). A humidified air flow of 40 ml/min is introduced at the base of the chimney and mixes with the column effluent of 20 ml/min that is ejected upward from three holes in the Teflon line. A 60 ml/min flow of helium and humidified air is not disturbingly fast to the nose, and the arrangement provides a reasonable standardization of dilution of the odorant carried from the gas chromatograph. Because the widths of chromatographic peaks are approximately the same when a programmed temperature rise is used, all compounds emerge with approximately the same dispersion in time and volume.

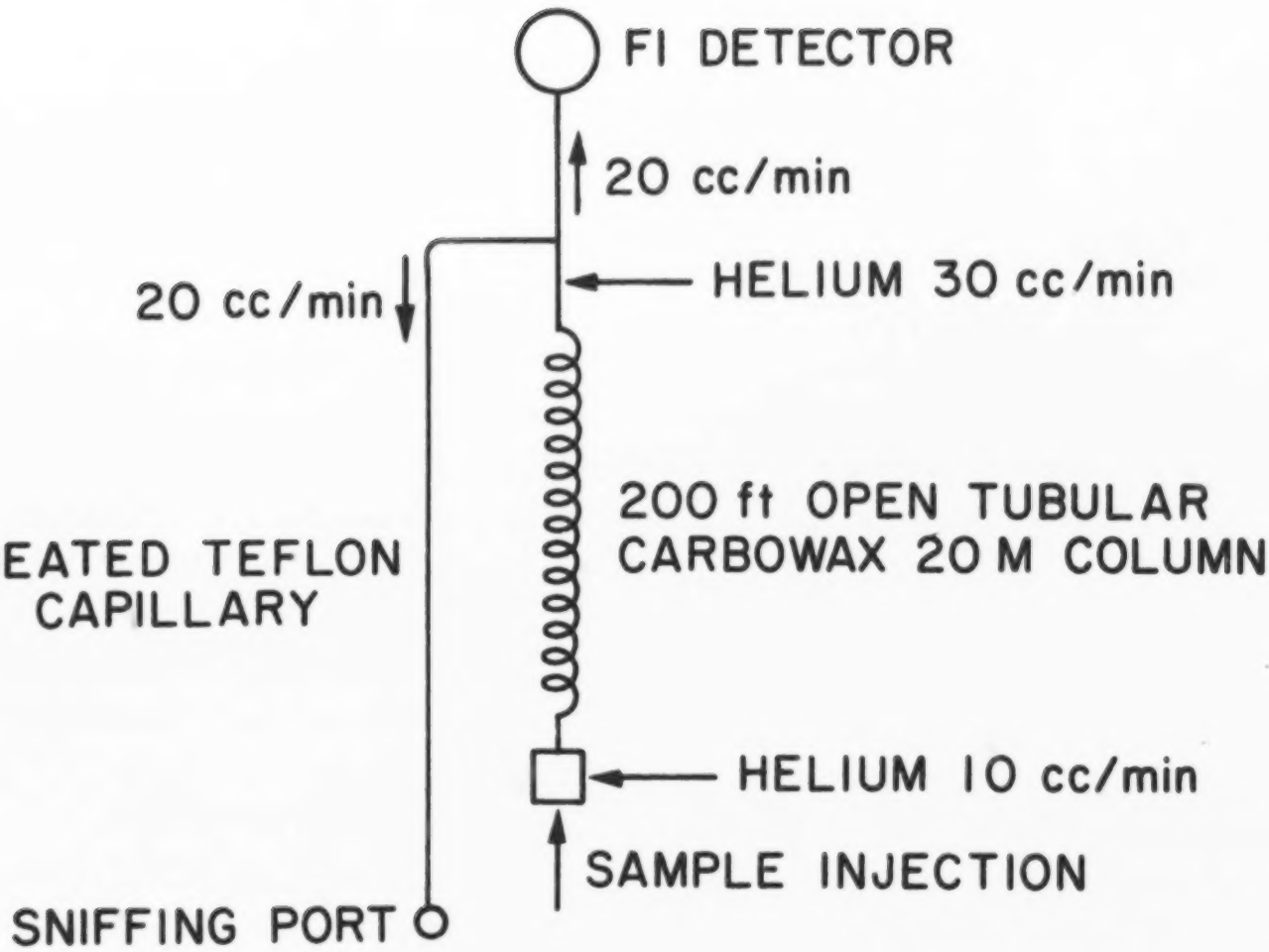

Figure D-1
SINGLE-COLUMN GAS-CHROMATOGRAPHIC FLOW ARRANGEMENT

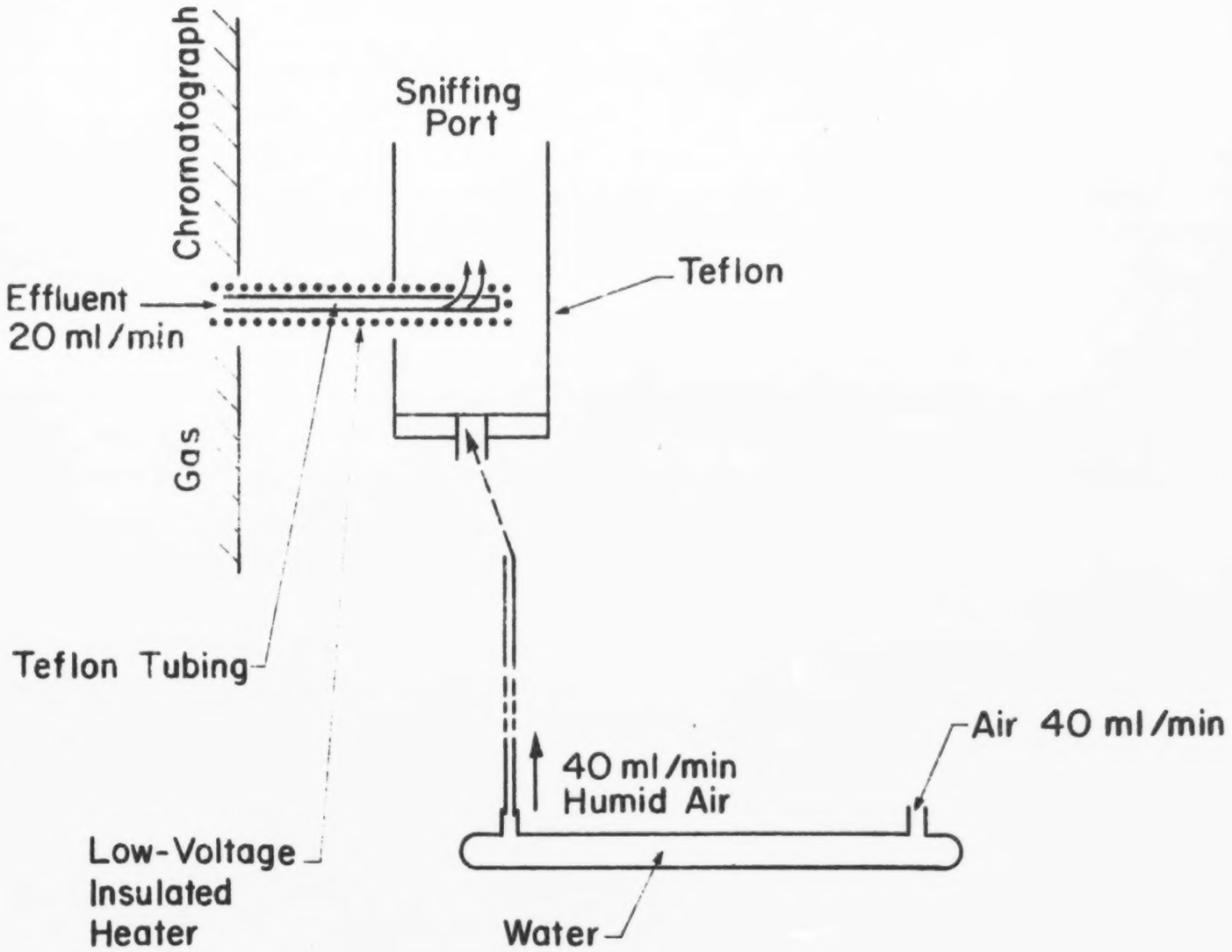

Figure D-2
SNIFFING PORT DESIGN

A schematic of the two-column system is shown in Figure D-3. For most of the exhaust sample analyses, the primary analysis column was a 200-ft SCOT column, 0.020" i.d., with Carbowax 20M stationary phase followed by a 50-ft Apiezon L SCOT column, 0.020" i.d. An injected sample passes through the first column at a helium flow rate of 10 ml/min. At the exit of the column, the effluent is split 1:1. One 5 ml/min portion is supplemented with 35 ml/min of helium and resplit, providing 20 ml/min flows to both a flame ionization detector and a sniffing port. The other half of the first column effluent travels to a secondary flow system where it is directed either onto the second analysis column or onto a similar dummy column. The injection of a peak from the continuous flow of primary column effluent onto the second column is accomplished with a three-way solenoid valve controlling an auxiliary helium input of 15 ml/min. The effluent switching itself is valveless. When the solenoid is switched on, 5 ml/min of helium is mixed with the 5 ml/min primary column effluent and the total directed onto the secondary analysis column, with the remaining 10 ml/min of auxiliary helium flowing through the dummy column. When the solenoid is off, the reverse occurs. The 10 ml/min helium-diluted primary column effluent flows through the dummy column,and 10 ml/min auxiliary helium passes through the analysis column. Thus, at all times, 10 ml/min flows pass through both columns in the secondary flow system. At the exit of the second analytical column, 30 ml/min of helium is added to the 10 ml/min column effluent,and the total is split so that 20 ml/min flows are provided for the second flame ionization detector and the second sniffing port. Considering the two portions of a particular amount of first column effluent, the one part reaches the detector at the same time the other part reaches the point of injection onto either of the two columns. Thus, the switching of the solenoid delineates the exact portion of first column chromatogram rechromatographed on the second column. In addition, since the primary column effluent is split 1:1,

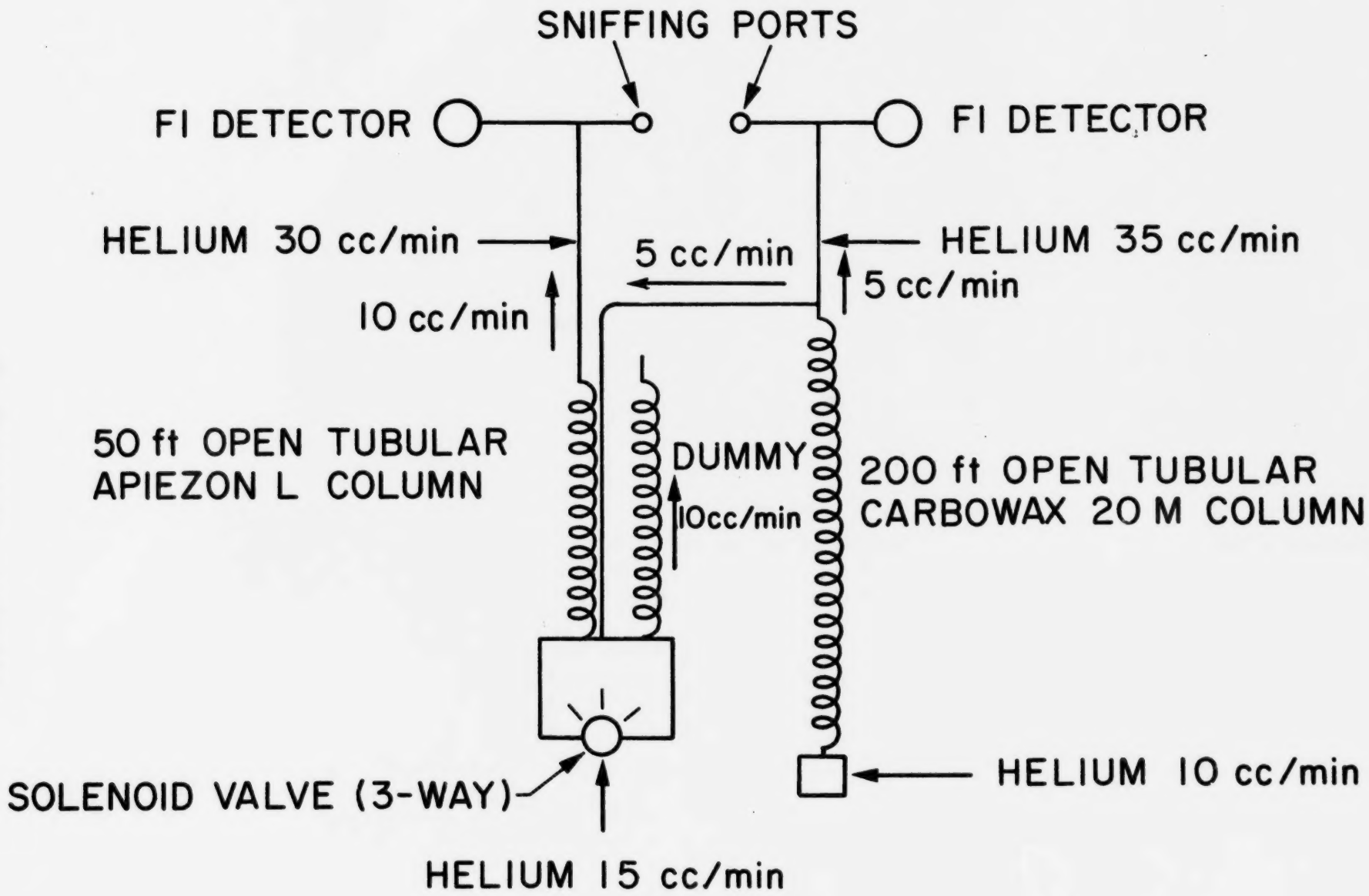

Figure D-3
DUAL-COLUMN GAS-CHROMATOGRAPHIC FLOW ARRANGEMENT

approximately equal concentrations reach the two sniffing ports and two detectors.

An estimate of total sample concentration and the concentrations of several individual components from the two-column instrument were obtained by electronic integration of peak areas using the Hewlett-Packard Model 3370 A integrator. The flame ionization detector response, which is essentially proportional to the weight concentration of organic material, was calibrated with a known mixture of methane in helium.

Appendix E

CHROMATOGRAPHIC DATA PROCESSING - THE KOVATS INDEX SYSTEM

Appendix E

CHROMATOGRAPHIC DATA PROCESSING - THE KOVATS INDEX SYSTEM

The problem of comparing absolute retention data collected from many experiments or even from many sources is greatly assisted by the use of the Kovats Index system.[1-5] Based on the fact that the logarithms of the retention times of the n-alkanes (corrected for the column dead volume) are a linear function of chain length, Kovats indexing is a logarithmic transformation of the corrected retention time of unknowns with respect to the corrected retention times of n-alkanes. By definition, the indexes of the n-alkanes are set equal to 100 times the number of carbon atoms (e.g., n-octane = 800, n-decane = 1000) and comprise the fixed points of the linear retention index scale from which unknowns are characterized.

The logarithmic function is applicable under isothermal conditions. When using linear temperature programming, however, the corrected retention times of the n-alkanes are an approximately linear function of chain length. To use Kovats Index notation for the data from the exhaust samples covering the range of C_6 through C_{16}, a calibration curve was obtained from the retention times of the internal standard n-alkanes with a computer program which performs a least squares semi-logarithmic fit. The curve is normalized to a straight line defined by a fifth order polynomial. From the calibration curve, the program then determines the Kovats Indexes of all other peaks in the chromatogram.

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(1) E. Kovats, Helv. Chim. Acta. 41, 1915 (1958).

(2) A. Wehrli and E. Kovats, ibid. 42, 2709 (1959).

(3) E. Kovats, Z. Anal. Chem. 181, 351 (1961).

(4) L.S. Ettre, "The Kovats Index Retention System," Anal. Chem. 36, 8, 31A (1964).

(5) E. Kovats, An. Gas Chromatography 1, 229 (1965).

The Kovats retention index system also provides a number of thermodynamically based rules that permit calculating the Kovats Index of a particular substance and thus predicting the positions of various homologs and derivatives. The principal rules are summarized as follows:

1. In an homologous series, the index increases by approximately 100 units per CH_2-group (exceptions are the lowest members of a series), and similar substitutions in similarly constructed compounds result in a similar increment of the indexes.
2. The index of an assymetrically substituted compound (e.g., X-R-Y) can be calculated as the mean of the two symmetrically substituted compounds (X-R-X and Y-R-Y).
3. The index of a non-polar substance remains almost the same in all stationary phases.
4. The index of any substance in various non-polar phases remains almost the same.
5. The difference in the indexes of two isomers in a non-polar stationary phase is approximately equal to a five-fold difference in their boiling points.
6. The difference between the indexes of a substance in a polar and a non-polar stationary phase is characteristic of the structure of the substance since it is an additive function of the various functional groups in the molecule, allowing for amount of screening of the functional groups by the structure of the molecule.

Appendix F

GAS CHROMATOGRAPH - MASS SPECTROMETER INTERFACING

Appendix F

GAS CHROMATOGRAPH - MASS SPECTROMETER INTERFACING

The apparatus for trapping specific components from the Apiezon L effluent of the two-column chromatograph, and subsequently releasing them for mass spectrometric analysis, was designed with 6 mil stainless steel tubing comprising the small volume system serving as the link between the two instruments. Ten individual trapping stations are provided by sets of hot and cold copper jaws in discrete positions on the 6 mil tubing.

Figure F-1 shows a portion of interface assembly with two of the trapping stations depicted. The point labeled A, representing a small volume Swagelok connection, is the point of attachment of the interface to either the GC or MS. The line is 6 mil tubing from point A to the liquid nitrogen cold trap. Teflon spacers, 0.0625" wide, between trapping stations hold the tubing securely in position. The grooves in the copper jaws provide good contact with the tubing, and spring levers position the jaws accurately and reproducibly in both hot and cold settings. The hot jaws are maintained at 180°C with cartridge heaters. The cold jaws extend into a Dewar of liquid nitrogen. Beyond the cold trap, the line continues to a tee with solenoid valves on each leg. Valve B, normally open, controls a helium input of 2 cc/min. The leg through valve C, normally closed, leads to a mechanical pump. At all times, except when actually trapping a peak, 2 ml/min of helium flows through the line.

In Figure F-2 the interface is shown connected to the gas chromatograph. The point of connection (A) is inside the chromatograph oven. From the point of connection to the first trapping station, Teflon-insulated nichrome wire is wound around the line to maintain the temperature at 180° to 200°C. The flow system of two-column chromatograph was slightly modified for trapping peaks with the interface. The 10 ml/min Apiezon L

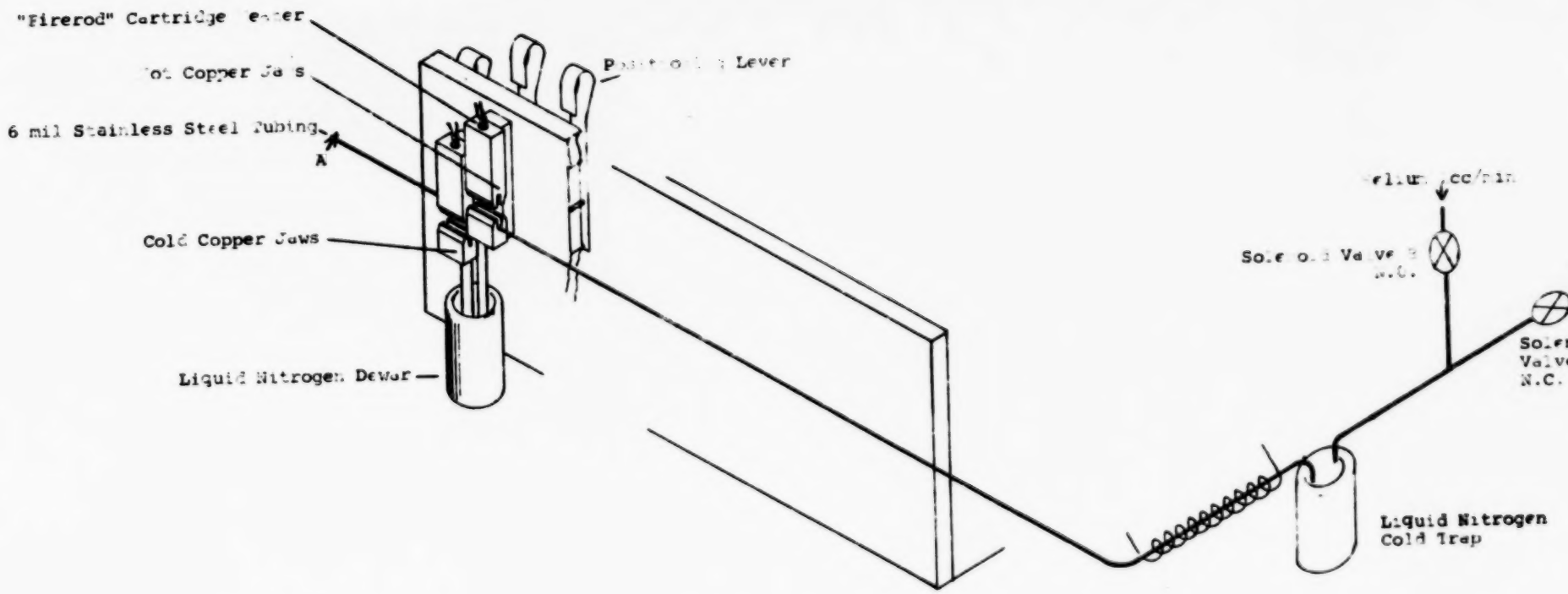


Figure F-1
MECHANISM FOR THE TRAPPING AND RELEASE OF COMPONENTS IN THE GC-MS INTERFACE

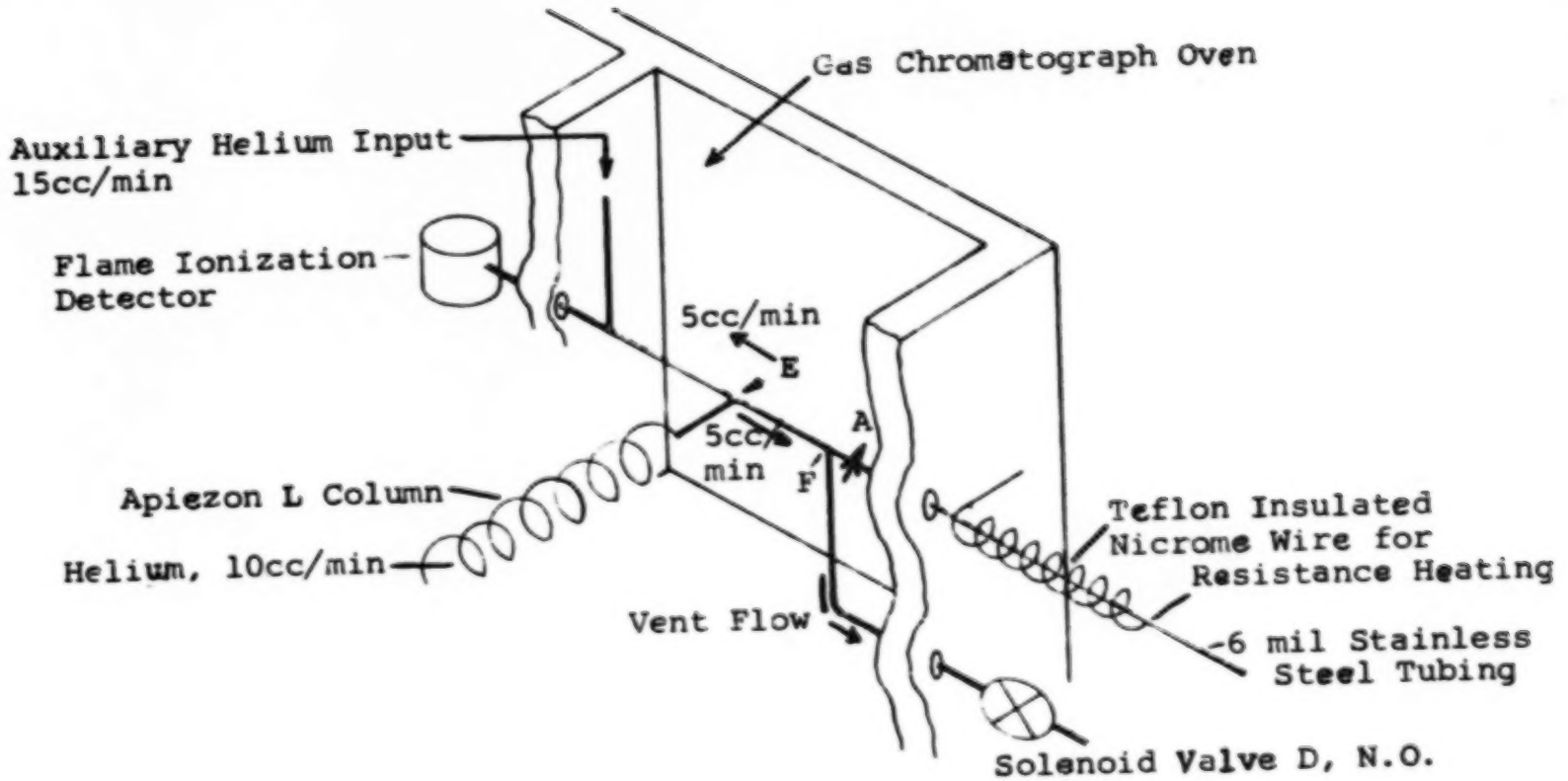


Figure F-2

INTERFACE CONNECTION TO THE TWO-COLUMN GAS CHROMATOGRAPH

column effluent is split 1:1 at point E on Figure F-2. One 5 ml/min portion is supplemented with 15 ml/min of auxiliary helium to provide a 20 ml/min flow to the detector as usual. The other portion of the effluent, along with the 2 ml/min flow from the interface line, is vented at point F on Figure F-2, except when trapping a peak. The flow through the venting line is controlled by solenoid valve D, normally open. Solenoid valves B, C, and D are activated by a common switch.

In the trapping operation, all hot jaws are initially on the transfer line and solenoids B, C, and D are off. When an Apiezon L peak is to be trapped, the cold jaws of a trapping station are positioned on the line, starting with the station furthest from the chromatograph. The three solenoid valves are switched on (valves B and D closed and valve C, to the pump, open), and the column effluent is drawn through the transfer line for the duration of the peak elution as shown on the Apiezon L chromatogram. The solenoids are then switched off, and helium again flows in the reverse direction through the transfer line and is vented along with the column effluent.

The assembly for joining the interface to the mass spectrometer is shown in Figure F-3. The interface line is attached at point A to a length of 6 mil stainless steel tubing extending through a flange bolted to the MS. Inside the MS, the tube is inserted into a pyrex tube spring positioned to deliver the sample directly into the ion chamber of the MS. The 6 mil tube is crimped, at point X on Figure F-3, to match the leak rate to the pumping speed of the MS.

A set of hot and cold jaws, identical to those used for injections into the chromatographs, provides the means for trapping peaks released from the interface line and subsequently injecting them into the MS in good peak shape. The sharp peak injections maximize the sample concentration available for mass spectral analysis. A 0.125 o.d. stainless steel tube sheathes the 6 mil tube to provide good contact with the grooves in the copper jaws.

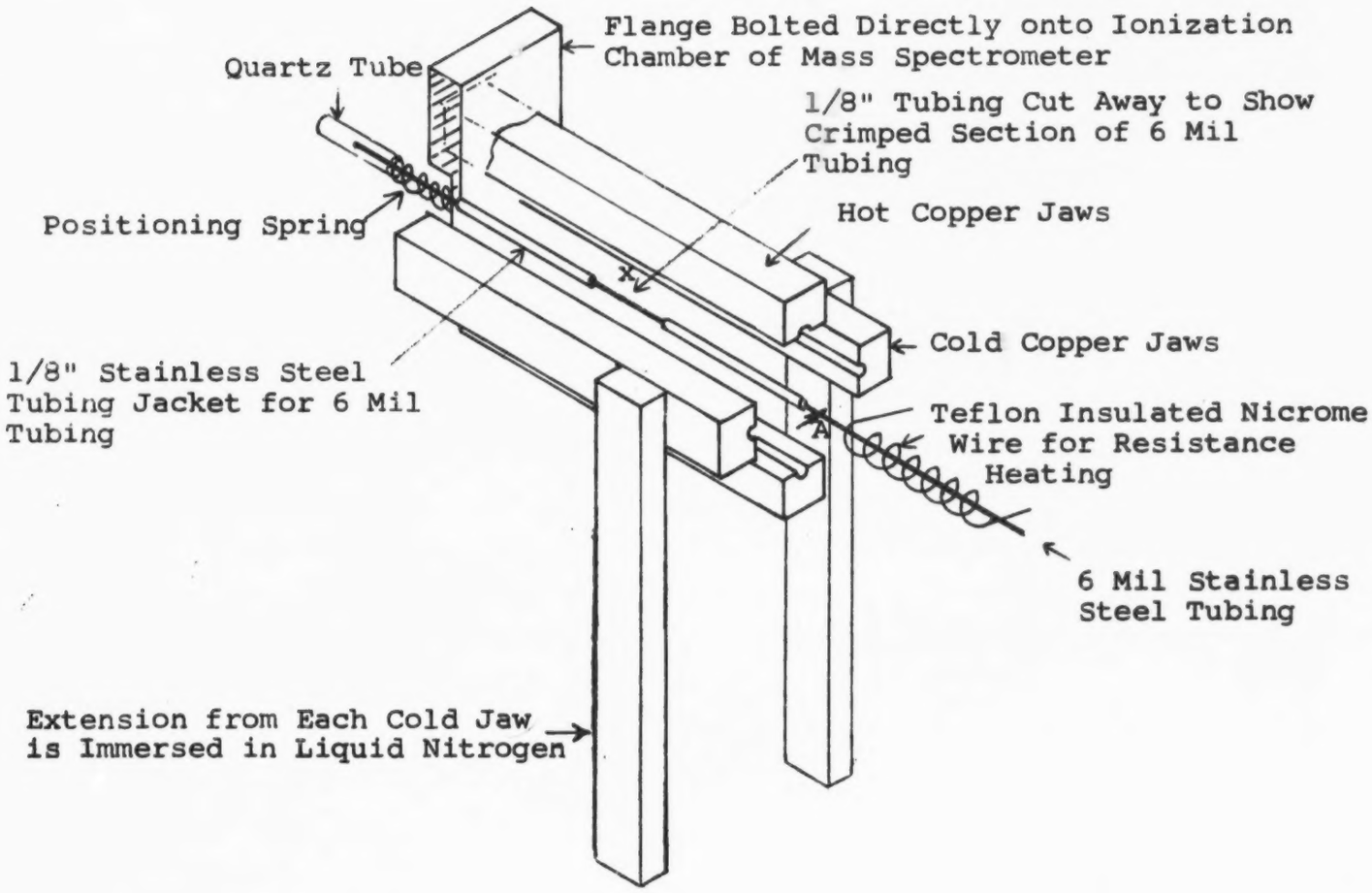

Flange Bolted Directly onto Ionization Chamber of Mass Spectrometer
Quartz Tube
1/8" Tubing Cut Away to Show Crimped Section of 6 Mil Tubing
Positioning Spring
Hot Copper Jaws
Cold Copper Jaws
1/8" Stainless Steel Tubing Jacket for 6 Mil Tubing
Teflon Insulated Nicrome Wire for Resistance Heating
6 Mil Stainless Steel Tubing
Extension from Each Cold Jaw is Immersed in Liquid Nitrogen

Figure F-3

DEVICE FOR SAMPLE INTRODUCTION INTO THE MASS SPECTROGRAPH

In operation, the set of cold jaws are positioned on the MS inlet tube, and the first component trapped in the interface (last trapped from the chromatograph) is released by removing the cold jaw at the trapping station and placing the hot jaw on the line. When the peak has been retrapped at the MS inlet, the cold jaws there are removed, and the hot jaws are placed around the tube to inject the peak into the MS. The efficiency of peak injection was tested by trapping a benzene peak from the GC and monitoring the principle ion peak, m/e 78, in the benzene spectrum after injection of the benzene into the MS. The recorder trace, shown in Figure F-4, indicated that samples are injected in good peak form.

With the interface system attached, the mass spectrometer operated at a vacuum of 2-3 x 10^{-6} mm Hg. For the exhaust sample analyses, the ionizing energy was set at 70 ev, accelerating voltage at 1800v for a mass range of ~2-600, and coil current usually set to scan up to 200 or 250 mass units. The resolution (M/ΔM) of the Hitachi Perkin-Elmer RMU-6D is 2000.

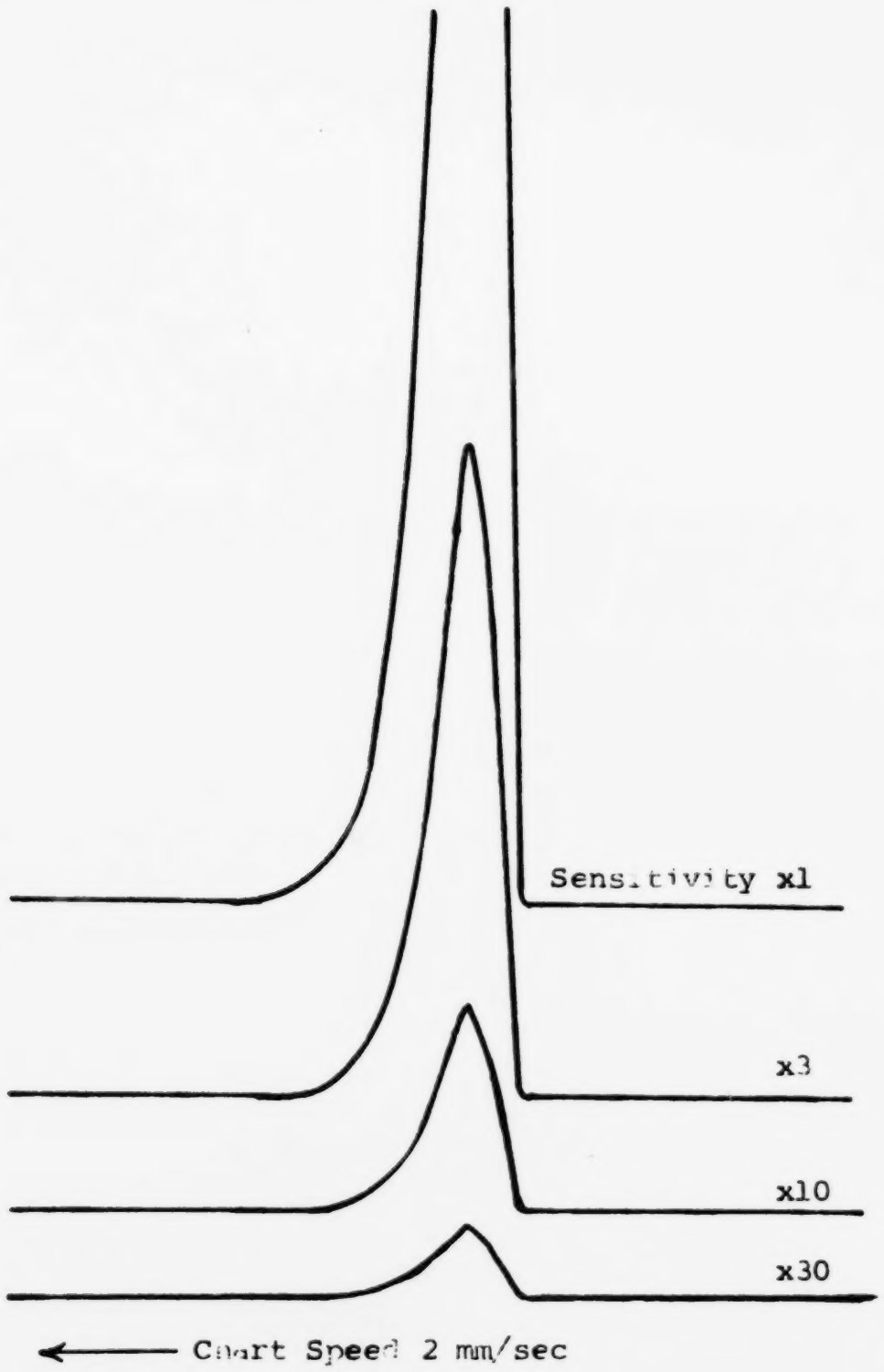


Figure F-4

RECORDER TRACE OF m/e 78 PEAK INTENSITY AFTER INJECTION OF BENZENE PEAK TRAPPED IN INTERFACE

Appendix G

MOLECULAR PROPERTIES FROM TWO-COLUMN CHROMATOGRAPHIC DATA

Appendix G

MOLECULAR PROPERTIES FROM TWO-COLUMN CHROMATOGRAPHIC DATA

The two-column analysis system results in data from which physicochemical properties of compounds can be estimated. In the two-dimensional plot of Carbowax 20M Kovats Index vs. corrected Apiezon L delay time, other molecular properties can be represented as the third dimension defining specific values of this third variable. The extent of the correlation was analyzed using the two-column data compiled from the known calibration compounds in a computerized regression program.

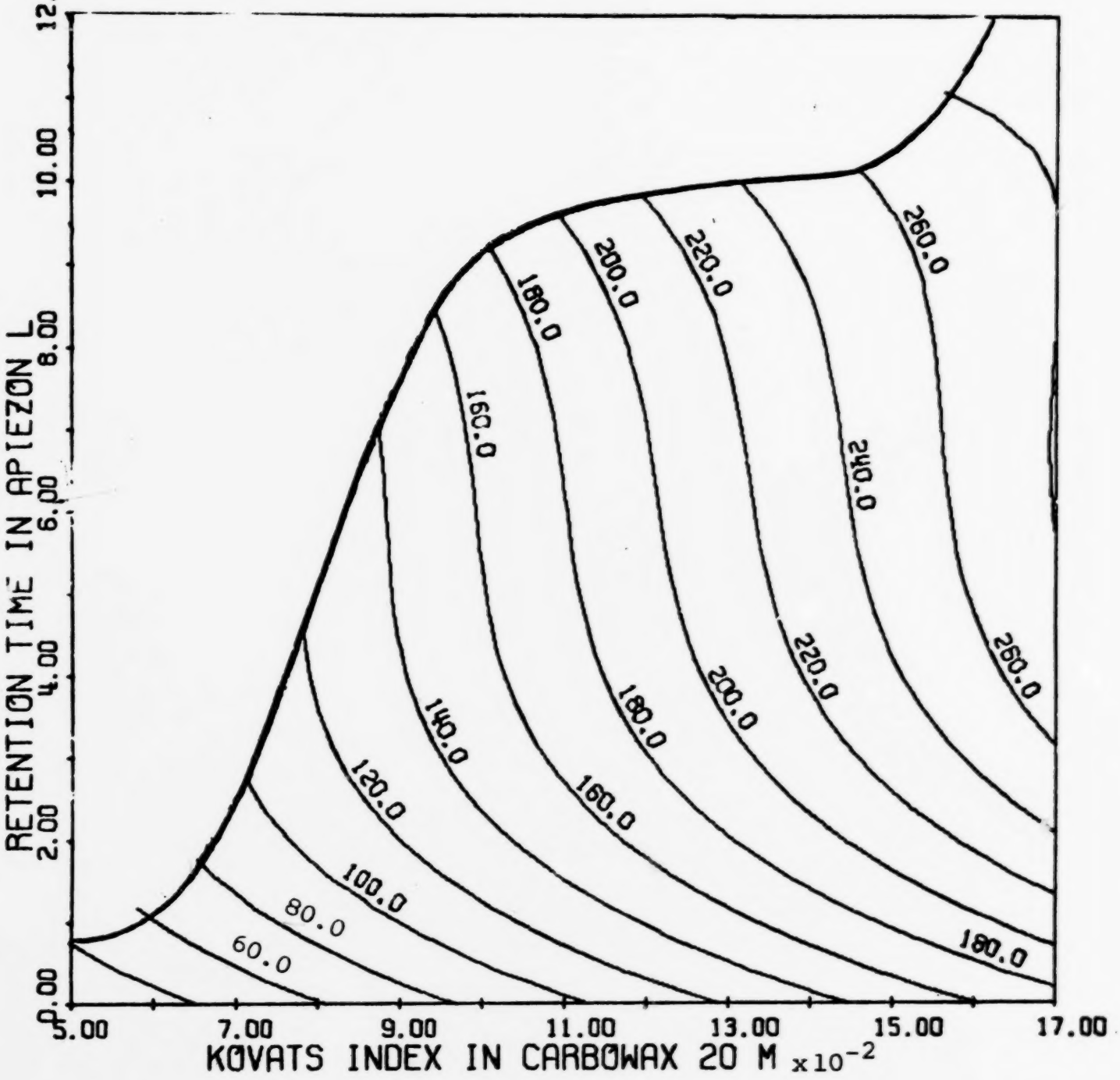
The computer program was BMD022 Stepwise Regression, Revision July 18, 1968, Health Sciences Computer Facility, UCLA. The two independent variables were: (1) Kovats Index in Carbowax 20M obtained under chromatographic conditions described in Section II; and (2) the delay in minutes in the Apiezon L column, corrected for column dead volume. The two variables were the X and Y coordinates in a plane with the dependent variable, $Z = F(X,Y)$, as a curved surface above the X-Y plane. The surface is expressed by a polynomial equation in which X and Y, their higher powers, and cross-terms of the various powers are used to form that Z plane for which the mean error of estimate for Z values is a minimum and the correlation coefficient is a maximum. A Calcomp plotter was used to plot curves connecting the points of equal Z values in the X-Y plane.

The Z's considered, pertinent to the diesel exhaust study, were boiling points and molecular weights. The correlation obtained between these molecular properties and the two-column data on known compounds is expressed by the following values of the resulting mean errors of estimate and correlation coefficients:

	Mean Errors of Estimate	Correlation Coefficient
Boiling Points	5.7°C	0.995
Molecular Weights	9.1	0.972

Figures G-1 and G-2 are the Calcomp plots of the iso-boiling point and iso-molecular weight curves, respectively.

These data complement the polarity-structure information provided by the retention difference obtained on the two-column chromatograph. The greater the number of defining parameters that can be applied to an unknown sample component peak, the more accurate are the conclusions regarding its probable identification. In addition, partial characterization of an unknown greatly assisted mass spectral interpretation.



PLOT OF 'BOILING POINT , DEGREES C'

Figure G-1

ISO-BOILING POINT CURVES FROM TWO-COLUMN CHROMATOGRAPH DATA ON KNOWN COMPOUNDS

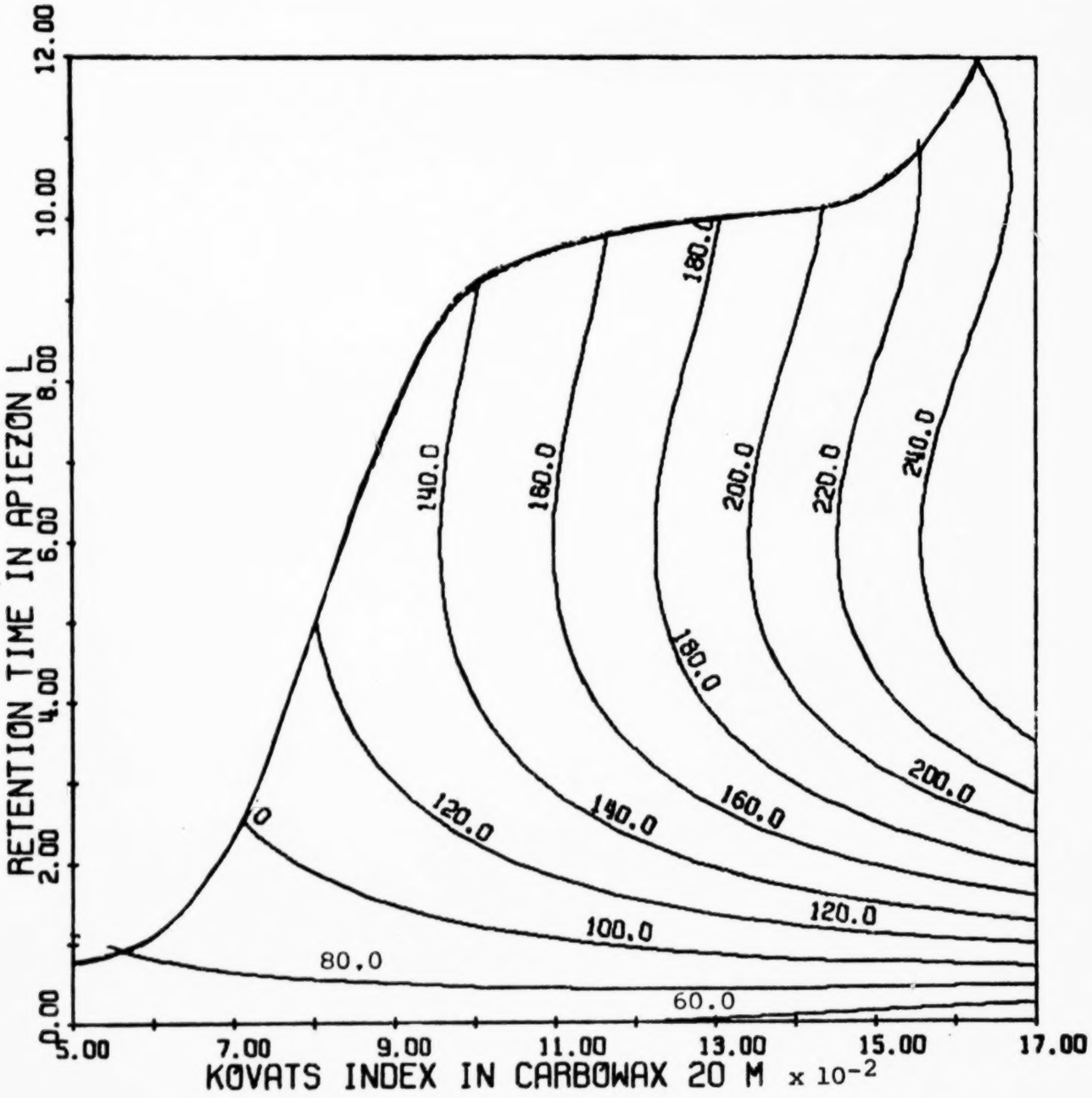


Figure G-2

ISO-MOLECULAR WEIGHT CURVES FROM TWO-COLUMN CHROMATOGRAPH DATA ON KNOWN COMPOUNDS